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DETERMINATION OF RATE CONSTANTS BY A DOUBLE-LINE FLOW INJECTION METHOD INCORPORATING A WELL-STIRRED TANK REACTOR

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Summary—Equations have been derived for the concentration–time profiles of reactants and products in a first order reaction obtained on passage of a reactant plug through a single well-stirred tank reactor. When taken together with the equations for physical dispersion of such a reactor under plug flow conditions, an expression for the reaction rate constant was derived which allowed its experimental determination in a relatively simple fashion. The method was tested for reactions between cerium and oxalic acid and between dichromate and ascorbic acid, for which values of the rate constants of around $2 \times 10^2 \text{ sec}^{-1}$ and $5.5 \times 10^3 \text{ sec}^{-1}$ were obtained. Good agreement with other experimentally determined values was obtained. The scope and the limitations of the proposed method are critically discussed with the aid of some model calculations. The range of values for which the method might be suitable is approximately 10^{-3} – 10^{-1} sec^{-1} . An equation analogous to a peak-width equation was derived as a further development of this approach. Good agreement with the previously determined values were obtained for both systems. The extension of the method to reactions other than first order is discussed.

Since its inception, flow injection (FI) techniques have been compared with and discussed as alternative to traditional 'batch' methods of chemical experimentation.¹ The general thrust of research in using flow injection techniques has been to improve methods of analysis and design new method of analysis. There has been some use of flow injection techniques as research tools, primarily in the determination of fundamental physical chemistry constants. Some examples of this work are the determination of diffusion coefficients,^{2–4} viscosity,^{2,5} formation quotients,^{6–13} chemical reaction orders¹⁴ and reaction rate constants (k),^{14–22} by FI methods

A number of methods have been used for the determination of reaction rate constants in flow injection systems. The problem is an interesting one because of the inherent kinetic nature of the flow injection process—the intercalation of one solution into a carrier stream in the absence of chemical reaction results in concentration gradients that define the FI peak. One approach to

determining rate constants have been to separate the kinetic contribution of the FI system from the progress of the reaction by monitoring the reaction (concentration vs. time) under conditions of stopped-flow. In this configuration the FI system is used as a means to mix reagents in precise proportions, and is similar to the traditional stopped-flow methods used to monitor fast reactions.²³ The determination of a rate constant by this procedure was first described by Kagenow and Jensen;¹⁵ Hungerford *et al.* described in detail the measurement of reaction rate constants by the stopped-flow method.¹⁶ Pseudo-first order and second-order rate constants for the oxidation of permanganate by benzaldehyde and crotonic acid were determined by the method.

The other FI methods for determining rate constants make use of a continuously flowing stream in which a reaction is occurring. An important difference between single-line and double-line manifolds needs to be noted. In a double-line manifold the reagent is added to the sample by merging at the confluence point and all elements of fluid of the dispersing sample zone are mixed with the same concentration of reagent. The concentration of reagent would be

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in excess at all times. However, in the single-line manifold, although the conditions may be chosen so that when the physically dispersed profiles of sample and reagent are viewed as they pass through the detector the reagent is in excess across the entire sample profile, this has not been the case during the time the sample and reagent have been in contact. Because the mechanism of mixing in a single-line manifold may be viewed as the penetration of the reagent from either end into the sample zone, the relative concentrations of sample and reagent in any element of fluid vary during the residence time in the system from sample excess to reagent excess. This will undoubtedly affect the rate of reaction which will, in general, vary in a complex fashion across the sample zone. As the most important parameter in governing the extent of mixing in a single-line manifold is the injected volume, this parameter can be viewed as a boundary condition affecting the measured value(s) of rate constants for single-line systems. Vanderslice and coworkers¹⁷ (single-line system) used the permanganate-benzaldehyde system as the model reaction in their continuous-flow FI method. The basis of the method was a modified diffusion-convection equation that contained a term for the first-order disappearance of sample. Measurement of peak height concentration (absorbance) of the injected KMnO_4 in the presence and absence of benzaldehyde was required for determination of the rate constant. A similar continuous flow method for determining k was proposed by Reijn and coworkers¹⁸ (single-line system) in a study of kinetics in a FI system containing a single-bead-string reactor. An equation for the calculation of the reaction rate constant from the reaction/no-reaction peak height ratio was derived using a tanks-in-series model. The product of the reaction between Cr(III) and edta was monitored in these experiments; pseudo-first order and second-order constants were calculated.

Valcarcel and coworkers^{14,19} (single-line closed loop system) have used an 'open-closed' FI system for the determination of reaction rate constants for the ligand-displacement reaction between cobalt(II)-ethyleneglycol bis-(β -aminoethyl ether)- N,N,N',N' -tetra acetic acid (EGTA) and 4-(2-pyridylazo)resorcinol (PAR). The dispersion of a slug of solution in a closed-loop was monitored under conditions of non-reaction and reaction. Data from both injections were used in the determination of the

rate constant. The reaction was studied under pseudo-first order conditions and under experimental conditions that resulted in higher reaction orders.

Other researchers have addressed the subject of kinetically slow reactions in flow injection systems. Mottola and coworkers^{20,21} (single-line system) have discussed the chemical contributions to dispersion in FI experiments. Data from numerical simulations and experiments were used to describe the dispersion of an injected slug of dichromate into ascorbic acid. Reaction rate constants were estimated from experimental data and were found to vary in an oscillating pattern. This is most likely due to the effect discussed earlier in relation to the relative concentrations of sample and reagent during the residence time. Hungerford and Christian²⁴ (single-line system) combined simultaneous dispersion and chemical reaction using an extended tanks-in-series model; they obtained good agreement between concentration-time profiles predicted by the model and experimental data obtained from the pseudo-first-order reaction between permanganate and crotonic acid. Hooley and Dessy²² (double-line system) also determined pseudo-first-order and second-order reaction rate constants for the reaction between KMnO_4 and KI as part of a demonstration of a FI system containing eight LED light sources. Data treatment was similar to that described above:¹⁴ the dispersion of the FI system was characterized and decoupled from data collected when KMnO_4 was injected into a KI reagent stream.

The well-stirred tank (WST) model has been used by Pardue²⁵⁻²⁷ and Tyson²⁸ in the derivation of equations describing the passage of a slug of analyte through a well-stirred tank reactor. The equations accurately describe the exponential 'rise' and 'fall' curves that define a FI peak. Jordan and Pardue²⁹ have recently shown that experimental concentration-time profiles are exactly those predicted by theory. Other work in the area of time-based FI methods has shown that time intervals predicted by the equations are accurate, even under non-WST conditions,³⁰ but the validity of the equations to accurately define the FI peak profile is limited under such experimental conditions. To achieve WST conditions, flow tubing must be minimized; short lengths of tubing are required to introduce the analyte into the tank and to connect the tank to the detector. In the above work,²⁵⁻³⁰ the chemical systems have

been rapid acid–base, oxidation–reduction and metal–ligand reactions.

In this paper a new continuous-flow FI method for determining pseudo-first order rate constants is described. The new method (hereafter termed the WST method) is based on data collected using a FI system containing a well-stirred tank. The theoretical basis of the method is also presented: equations that describe the passage of a slug of slowly-reacting solution through a WST are derived. The previously described WST model is modified for the condition of incomplete conversion of reactants to products during the passage of the injected slug through the mixing chamber. A relationship between the rate constant, the slope of the \ln absorbance *vs.* time plot, and parameters of the FI system is established. Data from the 'trailing' edge of the FI peak for two chemical systems—the reaction of cerium(IV) and oxalic acid and the reaction of dichromate and ascorbic acid—are used to determine rate constants; results are compared with k values obtained by traditional kinetics methods and FI stopped-flow kinetic methods. The range of rate constants applicable to the WST method are established by simulations.

EXPERIMENTAL

Modifications to the WST model

The derivation of equations that describe the passage of a slug of analyte through a WST with reaction follows the derivation previously described.²⁸ In that work equations were derived for the experimental situation of a flow of analyte through the tank without reaction and applied for chemical systems in which there were fast reactions; the product peak mimics the analyte peak for such reactions. The equations that define the leading edge of the FI peak contain a term for the flow of analyte into the chamber and a term for the removal of analyte at the same flow rate after instantaneous mixing. The equations that define the trailing edge of the FI peak contain a term for the removal of analyte from a peak (maximum) concentration. For the situation of a slow reaction, $C \rightarrow P$, the equations were modified by addition of a term for the first order removal of analyte, $-kC$. The slightly more complicated derivatives were integrated with the new term. A working equation for the determination of rate constants from kinetic data was obtained from equations that describe the trailing edge of the FI peak profile.

Simulations

Simulations of the concentration-time profile of flow injection peaks were programmed in QuickBasic (Microsoft). The following data were entered for an analyte concentration normalized to 1.0 or 0.6: mixing chamber or WST volume, volumetric flow rate, injection volume, first-order reaction rate constant and the time interval for data calculation. Time to peak maxima was established by the injection volume and flow rate. At each time (data point), the concentration of the analyte with no-reaction ($k = 0$), the concentration of the analyte with reaction, and the product concentration (difference between the no-reaction and reaction concentrations) were calculated and saved to a text file. The comma-delimited text files were changed to tab-delimited text files using Word 5.1 (Microsoft) and imported into a spreadsheet or graphing program.

Reagents

Choice of reactions. Model reaction systems had to fulfill the following three criteria: (1) the injected reactant must absorb in the UV/visible spectrum at a wavelength at which the product or other reagent does not absorb; (2) the reaction must follow pseudo-first-order kinetics; (3) the reaction must be slow enough for there to be a distinguishable difference between the concentration-time profiles of the no-reaction and reaction experiments, but be fast enough that the reaction can occur on the time-scale of a typical flow injection experiment in which the peak flows through the detector in, at most, 5 min. The first two criteria are imposed by the model: equations are derived for removal of the injection solution and only for the situation of first-order kinetics.

Cerium(IV)–oxalic acid. The oxidation–reduction reaction between (Ce(IV) and oxalic acid can be followed spectrophotometrically by monitoring the yellow Ce(IV)–sulfate complex. In acidic solution, the rate of the reaction was sufficiently rapid for the experiment. The mechanism of the reaction is reasonably complex; the rate expression for the overall reaction in sulfate media has been established by Rechnitz and El-Tantawy:³¹

$$-\frac{d[\text{Ce}(\text{SO}_4)_3^{2-}]}{dt} = \frac{K[\text{Ce}(\text{SO}_4)_3^{2-}][\text{H}_2\text{C}_2\text{O}_4]}{[\text{H}^+][\text{HSO}_4^-]} \quad (1)$$

in which K is the product of the rate constants of the individual steps of the reaction. By

performing the reaction at constant ionic strength and constant pH, and by maintaining a constant excess of oxalic acid, the rate expression reduced to a pseudo-first order one:

$$\text{rate} = -\frac{d[\text{Ce}(\text{SO}_4)_3^{2-}]}{dt} = k_{\text{app}}[\text{Ce}(\text{SO}_4)_3^{2-}] \quad (2)$$

for which the apparent rate constant, k_{app} , can be determined experimentally.

Ce(IV) and oxalic acid solutions were prepared in a buffer solution consisting of 0.4M H_2SO_4 and 0.4M Na_2SO_4 (total $[\text{SO}_4^{2-}] = 0.8\text{M}$). A $3.231 \times 10^{-2}\text{M}$ oxalic acid solution was prepared from the solid acid and a $1.375 \times 10^{-3}\text{M}$ cerium(IV) solution was prepared from ceric ammonium nitrate salt. All solutions were purged with argon.

Dichromate-ascorbic acid. The oxidation-reduction reaction between dichromate and ascorbic acid was similarly followed by monitoring the conversion of yellow $\text{Cr}_2\text{O}_7^{2-}$ to Cr(III). In acidic solution the reaction was too fast for the WST method, but in neutral to slightly basic solution, the reaction rate was much less rapid. The rate law also reduces to a pseudo-first order expression,

$$\text{rate} = -\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k_{\text{app}}[\text{Cr}_2\text{O}_7^{2-}] \quad (3)$$

by use of a KH_2PO_4 buffer and by maintaining the ascorbic acid concentration at a constant excess. Reagents were prepared in 0.1M KH_2PO_4 buffer (pH 8.1). A $2.632 \times 10^{-2}\text{M}$ ascorbic acid solution was prepared from the dry acid; a $4.664 \times 10^{-4}\text{M}$ dichromate solution was prepared from KCr_2O_7 . Solutions were also purged with argon gas.

FI system

A double-line flow injection manifold was used in the experiments to determine rate constants (Fig. 1). The system consisted of two peristaltic pumps (Ismatec sa), a pneumatic valve for timed-injections (P.S. Analytical), a confluence point (Perkin-Elmer), a well-stirred mixing tank with magnetic follower and a UV/visible spectrometer (Hewlett Packard 8452A diode array with kinetic software). Perkin-Elmer yellow/blue/yellow (0.06 in i.d.) peristaltic pump tubing was used in the three flow lines. Teflon flow tubing (0.8 mm i.d.) was used to make connections between valve, confluence point, mixing chamber and the flow cell (8 μl , Hellma) The length of tubing between both the confluence point and the mixing

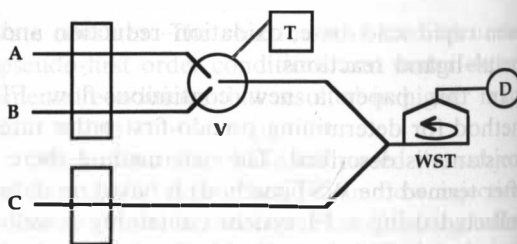


Fig. 1. Schematic of the flow injection manifold. A, B, and C = solutions (see text); V = pneumatic valve; T = timer (connected to V); WST = well-stirred tank; D = detector (flow cell in spectrophotometer). Timed-injections are performed by turning V from flow line B (buffer solution) to flow line A (metal solution).

chamber and the mixing chamber and the detector was minimized (10 and 35 cm, respectively). The 1170 μl WST was constructed from perspex and has been described previously.³² Constant temperature was maintained with a water bath (Fisher), which was used to pump thermostatted water through a water-jacketed cell holder (Hewlett Packard). A timing circuit designed to actuate the pneumatic valve after a preset time interval was constructed in-house.

Procedures

WST FI method. For each chemical system, the species being monitored in the reaction was introduced (via flow line A) into flow line B (buffer solution). Flow line A/B merged with flow line C at the confluence point (C). The absorbance-time profile was established for the passage of the slug of the metal species through the WST under conditions of no-reaction (buffer in line C) and reaction (reagent in line C). The solutions used in the flow lines and other experimental conditions are noted in Table 1. The injection volume was established by the time interval that the pneumatic valve was turned and the flow rate in line A. Flow rates were measured by the weight of water collected over several minutes. Temperature was maintained to within 0.1°C over the course of the experiments; solutions were immersed in the water bath for 15 min prior to experimentation. Timed-injections were accomplished by manually synchronizing the start of the timer with the opening of the shutter of the spectrophotometer.

Absorbance-time data were collected from the trailing edge of the FI peak: nine to 11 points were selected in the time interval from the peak maxima to approximately 0.05 absorbance above the baseline. Transformation of data (calculation of \ln absorbance and adjustment

Table 1. Experimental conditions

Chemical system	Solin in flow line A (λ monitored)	Solin in flow line C (no rxn./rxn.)	Injection volume (μl) (Inj. time @ Q in line A)	Flow rate (Q) through tank ($\mu\text{l}/\text{sec}$)	Theoretical (Q/v)(sec^{-1}) ($V = 1167 \mu\text{l}$)	Temperature of water bath ($^{\circ}\text{C}$)
Cerium/oxalic acid	Cerium(IV) (416 nm)	Buffer/ oxalic acid	670 (50 sec @ 13.4 $\mu\text{l}/\text{sec}$)	26.9	2.30×10^{-2}	20.8
Dichromate/ascorbic acid	Dichromate (414 nm)	Buffer/ ascorbic acid	959 (70 s @ 13.7 $\mu\text{l}/\text{sec}$)	27.4	2.35×10^{-2}	22.3

for absorbance at infinite time) was performed using Excel 2.2 (Microsoft). Regression equations for \ln absorbance vs. time plots were obtained using CricketGraph 1.3 (Cricket Software). Times from the start of data collection were plotted in lieu of plotting the corrected times from peak maximum; this is possible because the slope (and rate constants) are independent of the value of the y -intercept.

Other methods. Two other methods for determining pseudo-first-order rate constants were used to confirm the results of the WST flow method: a FI stopped-flow method and a standard cuvette method. For both methods the temperature of the water bath and wavelength at which the reaction was monitored were the same. Data was treated in the same manner as described above.

For the FI stopped-flow method, the procedure for the WST method was followed with the exception of the flow being stopped at some time on the trailing edge of the FI peak. Stop times were approximated with a stop watch. Data was not collected for the no-reaction experiment, except to confirm that the reagent did not react with the buffer. In the cuvette method the reagent (oxalic or ascorbic acid) and buffer were placed in the cuvette with a stir bar. After data collection was begun, the metal species was introduced into the cuvette by one-ml pipette. Concentrations were established such that the same amount of reagent in flow line C of the WST method was present in the cuvette (to account for 1:1 dilution at the confluence point).

RESULTS AND DISCUSSION

Equations and simulations

Equations that were derived with the modified well-stirred tank model are listed in Table 2; terms in Table 2 and in the following discussion of results are enumerated in Table 3. The previously derived equations for the situation of non-reaction (or for a fast reaction) are listed in Table 2 for reference. Equations on the right-hand side of Table 2 ('slow reaction') reduce to those of the left side ('no reaction') when $k = 0$.

Simulated FI peaks (Fig. 2) illustrate the effect of including a term for removal of sample by reaction in the WST model. For a rate constant of 0.01 sec^{-1} the FI concentration-time profile mimics that of the peak with no reaction, but at larger k (0.1 sec^{-1}), the

Table 2. Equation describing the passage of a slug of solution (concentration *vs.* time) through a well-stirred mixing device under conditions of 'no-reaction' and 'reaction'.

No-reaction ²⁸	Eqn.	Reaction	Eqn.
Leading edge of peak $C = C^o(1 - e^{-\frac{Q}{V}t})$	4	$C = \left(\frac{Q}{Q + kV}\right)C^o(1 - e^{-\frac{Q+kV}{V}t})$	5
Peak maximum $C^p = C^o(1 - e^{-\frac{V_i}{V}})$	6	$C^p = \left(\frac{Q}{Q + kV}\right)C^o(1 - e^{-\frac{V_i}{V} + kt_p})$	7
Trailing edge of peak $C = C^p e^{-\frac{Q}{V}(t - t_p)}$	8	$C = C^p e^{-\frac{Q+kV}{V}(t - t_p)}$	9

The 'reaction' equations reduce to the 'no-reaction' equations when $k = 0$. The equations that describes the concentration-time profile of a fast reaction ($k > 0.5 \text{ sec}^{-1}$) are the same for 'no-reaction' if the product profile is monitored.

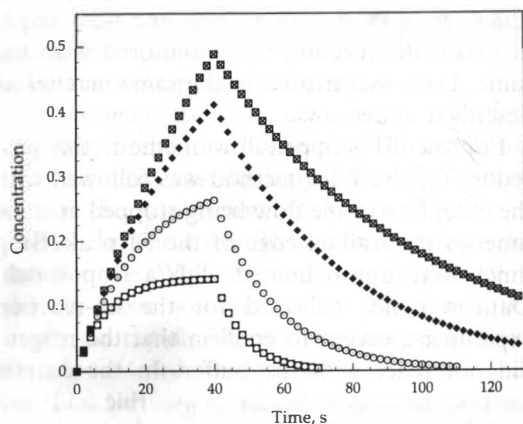


Fig. 2. Simulated flow injection peaks. Parameters of simulations: $V = 1500 \mu\text{l}$; $V_i = 1000 \mu\text{l}$; $Q = 25 \mu\text{l sec}$; $C^o = 1.0$. Data collected every 2 sec for rate constants of 0.00 sec^{-1} (no-reaction, \square), 0.01 s^{-1} (\blacklozenge), 0.04 s^{-1} (\odot) and 0.10 s^{-1} (\square with a dot).

leading edge of the peak profile is distorted. For all k , times to peak maxima (t_p) are the same. In Fig. 3 a comparison of experimental data with simulated data shows that the model is a

reasonable one to use for these experiments. Differences between the simulated and experimental trailing edge of the FI peak are negligible. The t_p of the experimental FI peak in Fig. 3 was shifted approximately 9 sec in order to line-up the C^p . The delay time is a result of the flow tubing that is required to connect the WST to the other components of the FI system.

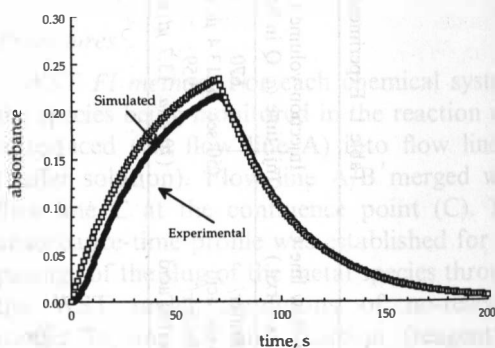


Fig. 3. Comparison of experimental and simulated absorbance-time profiles for the dichromate-ascorbic acid system. Experimental parameters are listed in Table 1.

Table 3. List of symbols used in equations (4)-(17)

Symbol	Definition
C	Concentration of sample at any time
C^o	Concentration of undiluted sample (concentration before injection).
C^p	Concentration of sample at peak maximum (also C_p)
C_{nr}^p	Concentration of sample at peak maximum for no-reaction experiment.
C_r^p	Concentration of sample at peak maximum for reaction experiment.
k	Pseudo-first-order reaction rate constant.
m	Slope of \ln absorbance <i>vs.</i> time plot.
Q	Volumetric flow rate.
t	Time from start of data collection, or from time at peak maximum.
t_p	Time at peak maximum (C^p).
t_{nr}	Time on peak profile for no-reaction experiment.
t_r	Time on peak profile for reaction experiment.
Δt	Time interval between time on no-reaction and reaction curves at certain C .
V	Volume of well-stirred tank.
V_i	Volume of sample injected.
$(Q/V)_{ex}$	Experimentally determined constant of the FI system.
$(Q/V)_{th}$	Theoretically determined constant of the FI system.
n	Order of chemical reaction.

The model equations were derived under the assumption that there is no connecting tubing between the confluence point (or injection valve) and the mixing chamber and the mixing chamber and the detector (see Experimental section).

Working equation

The basis of the WST FI method is the rearrangement of equation (9) into an equation from which plotted data can be used to determine k . Substituting t for $(t - t_p)$ and taking the natural logarithm of both sides of the equation, transforms equation (9) into a form that can be readily plotted:

$$\ln\left(\frac{C}{C^p}\right) = -\left(\frac{Q + kV}{V}\right)t. \quad (10)$$

A plot of $\ln(C/C^p)$ vs. t (or $\ln C$ vs. t) yields a slope,

$$m = -\left(\frac{Q + kV}{V}\right). \quad (11)$$

Thus, the reaction rate constant can be determined by the sum of a term for the slope of the $\ln(\text{absorbance})$ vs. time plot and a term that is characteristic of the experimental conditions.

$$k = -[m + (Q/V)]. \quad (12)$$

The (Q/V) term can be obtained experimentally by plotting $\ln(\text{absorbance})$ vs. time for the no-reaction experiment (slope = $-(Q/V)_{\text{ex}}$) or from known experimental conditions ($(Q/V)_{\text{th}}$).

The same procedure was used to develop a working equation from equation (5) for data obtained from the leading edge of the FI peak:

$$\ln\left[1 - \left(\frac{Q + kV}{Q}\right)\frac{C}{C^o}\right] = -\left(\frac{Q + kV}{V}\right)t. \quad (13)$$

A plot of the left-hand side of equation (13) vs. time has the same slope (equation 11) as a plot of equation (10); rate constants can be determined by the procedure described for

data obtained from the trailing edge of the FI peak.

Results for determination of k

Results from the experiments to determine k for the reactions between cerium(IV) and oxalic acid and dichromate and ascorbic acid are listed in Tables 4 and 5. Rate constants obtained by the WST FI method were calculated using both $(Q/V)_{\text{th}}$ and $(Q/V)_{\text{ex}}$. Results for the cerium-oxalic acid system show that there is no statistical difference at the 95% confidence level between the three methods. Results for the dichromate-ascorbic acid system show that there is no statistical difference for k determined using the $(Q/V)_{\text{th}}$, but that there is a statistical difference for k determined using $(Q/V)_{\text{ex}}$. The confidence interval for k determined using the continuous flow FI method was twice as large as for the other methods. For this reaction the rate constant was calculated from the difference in two 10^{-2} sec^{-1} quantities [m and (Q/V)]. It is not surprising that the uncertainty in the method is higher than the cerium-oxalic acid system in which $k \approx 2 \times 10^{-2} \text{ sec}^{-1}$.

A sample plot of kinetic data for the cerium-oxalic acid system is illustrated in Fig. 4. The difference between the slopes of the non-reaction and reaction plots is the result of the removal of sample by reaction. In the WST FI method the trailing edge of FI peak profile is the result of the combined effect of the removal of sample by both flow and reaction. Despite this complication, data is handled in the same manner as that of the standard kinetic methods—a plot of $\ln(\text{absorbance})$ vs. time. The simplicity of this approach to data treatment is possible as a result of the first-order reaction imposed on the first-order wash-out of sample from the WST (see equation 8).

A facet of the traditional handling of kinetic data for which the current WST model does not account is absorbance at infinite time (A_∞). Use of A_∞ obtained from the FI stopped-flow method is not valid because of the continuous

Table 4. Results from cerium-oxalic acid experiments

Method	Rate constant, $\times 10^2 \text{ sec}^{-1}$ ($\pm 95\%$ CI)
Cuvette/batch*	2.07 \pm 0.09
Flow injection, stop-flow*	2.01 \pm 0.06
Flow injection, WST†	2.08 \pm 0.10
Flow injection, WST‡	1.94 \pm 0.10

* $n = 3$.

† $n = 4$, $(Q/V)_{\text{ex}}$ used: $2.16 \times 10^{-2} \text{ sec}^{-1}$.

‡ $n = 4$, $(Q/V)_{\text{th}}$ used: $2.30 \times 10^{-2} \text{ sec}^{-1}$.

Table 5. Results from dichromate-ascorbic acid experiments

Method	Rate constant, $\times 10^3 \text{ sec}^{-1}$ ($\pm 95\%$ CI)
Cuvette/batch*	5.48 ± 0.09
Flow injection, stop-flow*	5.50 ± 0.08
Flow injection, WST†	4.89 ± 0.20
Flow injection, WST‡	5.51 ± 0.20

* $n = 4$.

† $n = 5$, $(Q/V)_{\text{ex}}$ used: $2.41 \times 10^{-2} \text{ sec}^{-1}$

‡ $n = 5$, $(Q/V)_{\text{th}}$ used: $2.35 \times 10^{-2} \text{ sec}^{-1}$.

removal of product from the WST. Equations could be modified by inclusion of a term that accounts for the absorbance of a second species (product) over the concentration-time profile. In this work, A_{∞} is small for both chemical systems and thus, has little effect on the results. For the cerium-oxalic acid system, $A_{\infty} = 0.00$; for the dichromate-ascorbic acid system, $A_{\infty} = 0.025$ as measured by the stopped-flow method. This term was subtracted from absorbance data prior to the preparation of $\ln(\text{absorbance})$ vs. time plots for the cuvette and stopped flow methods.

Range of rate constants

The range of first-order rate constants that can be measured by the WST FI method were estimated from simulated data. The rate constants are limited on the high end when the FI peak profile is indistinguishable from the baseline and on the low end when the FI peak profile is indistinguishable from the no-reaction profile (see Fig. 2). An absorbance of 0.05 was chosen as the minimum absorbance above the baseline for the faster reactions such that several data points can be obtained prior to the FI profile merging with the baseline; an absorbance of 0.005 was chosen as the minimum difference

between no-reaction and reaction profiles for slower reactions. With these criteria a range of $5 \times 10^{-4} \text{ sec}^{-1}$ to $3 \times 10^{-1} \text{ sec}^{-1}$ was established. Considering difficulties that arise as a result of experimental error (e.g. the dichromate-ascorbic acid system), a more realistic range is 1×10^{-3} to $1 \times 10^{-1} \text{ sec}^{-1}$.

Features and limitations of the WST method

The well-stirred tank FI method has some interesting features and some limitations. Unlike FI methods in which the no-reaction FI profile must be established,^{20,23} in the WST method k can be determined with data from a single injection if Q and V of the FI system are known. Data handling is comparable for all methods and the speed of analysis is comparable to other continuous-flow FI methods. The stopped-flow methods require more time only for slow reactions; this is not a disadvantage because of the broad range of k that can be determined.

The use of the well-stirred tank reactor leads to the development of simple and accurate equations for the physical dispersion processes in the flowing stream; thus, the equations for the combined processes of dispersion and reaction can be described without the need for numerical methods or approximations. Attempts to model these processes for flow in an open tubular reactor have not been particularly successful (see example Fig. 4 of Ref. 33).

The WST method can be further simplified by eliminating timed-injection. Timed-injection is not required as a result of the manner in which data is collected on the trailing edge of the FI peak. This is similar to all kinetic methods in which k is determined from the slope of a $\ln(\text{absorbance})$ -time plot—the initial concentration of sample (C^p in the above experiments) does not have to be known for the slope to be accurately determined.

The use of the double-line manifold established a fixed initial reagent concentration over

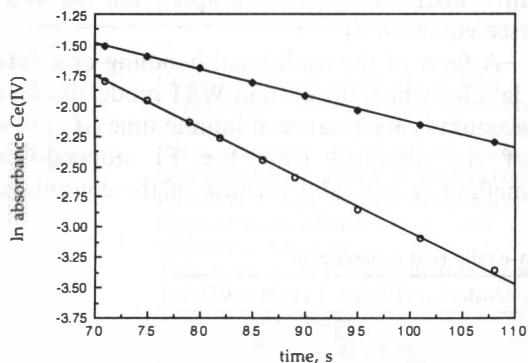


Fig. 4. Kinetic plots for the cerium(IV)-oxalic acid system. Plots of the natural logarithm of absorbance vs. time for experiments with oxalic acid (reaction, O) and without oxalic acid (no-reaction, ◆). Equations for the regression lines are noted.

the entire sample FI peak. Thus, the pumped reagent concentration does not need to be in great excess over the injected sample concentration in order for pseudo-first-order reaction conditions to prevail as the sample concentration is decreased by passage through the well stirred tank. In the experimental procedure used here, data is taken from the washout and thus if the concentrations are selected so that the relative values are appropriate at the start of the experiment (the peak maximum, where the reagent to sample concentration ratio is at a minimum), then at all subsequent points there will be a greater excess of reagent over sample. In the stopped-flow or other 'batch' methods, in which the evolution of fixed initial concentrations with time are followed, pseudo-first-order conditions are fixed by a minimum 10-fold excess of reagent²³ (though this value depends on the rate of the reaction, slower reactions consume less reagent). This may place limitations on the time interval over which valid data can be collected and can be a difficult experimental condition to achieve when solubility of the reagent is low.

The range of applicable rate constants is a limitation of the WST method; the stopped-flow method can be used to determine k that are several orders of magnitude less than the lower limit of 10^{-3} sec^{-1} established above. Based on published work,^{14,17,18,21,22} the range of k that can be determined by the WST method is equivalent to all continuous FI methods.

Determination of k by measurement of Δt

Despite the successful way in which the kinetic contribution of the reaction has been decoupled from the overall FI peak, the WST method requires as much handling of data as a FI stopped-flow experiment. Rearrangement of the equations that describe the no-reaction and reaction FI peak profiles (equations 8 and 9) leads to an equation for which the rate constant can be determined from the measurement of time on the peak profiles. Measurement of k by this procedure is similar to the use of time intervals on FI peaks (including the interval of time between doublet peaks) as a quantitative analytical parameter.^{25,28}

By setting equations 8 and 9 equal at a concentration, C , at any time past C^p , the following relationship is established:

$$C_{nr}^p e^{-\left(\frac{Q}{V}\right)(t_{nr}-t_p)} = C_r^p e^{-\left(\frac{Q+kV}{V}\right)(t_r-t_p)}, \quad (14)$$

for which t_{nr} and t_r are times at an arbitrary C for the no-reaction and reaction experiments and t_p does not vary between experiments (see Table 2 for other symbols). By taking the natural logarithm of both sides and by rearranging equation (14), an equation for determining k is obtained:

$$k = \frac{\left(\frac{Q}{V}\right)(t_{nr}-t_r) - \ln(C_{nr}^p/C_r^p)}{(t_r-t_p)}. \quad (15)$$

Data from the above experiments were used to verify the applicability of equation (15). The determined rate constants for the cerium-oxalic acid system were within the previously established confidence intervals of the method (Table 4): for example at an absorbance of 0.052, $t_{nr} = 143 \text{ sec}$ and $t_r = 98 \text{ sec}$; k was calculated to be $2.025 \times 10^{-2} \text{ sec}^{-1}$. For this system, equation (15) was adjusted to account for the situation of t_p varying between experiments. The k for the dichromate-ascorbic acid experiment were consistently low as compared to the results in Table 5: for example, a rate constant of $4.675 \times 10^{-3} \text{ sec}^{-1}$ was obtained using $t_{nr} = 164.5 \text{ sec}$ and $t_r = 145.5 \text{ sec}$ (absorbance of 0.04) with $t_p = 84 \text{ sec}$ for $C_{nr}^p = 0.2582$ and $C_r^p = 0.2582$ and 0.2157 , respectively. The error was attributed to the imprecision in (Q/V) . Although data collection and data handling is reduced, the terms in equation (15) must be known precisely. Times and parameters of the FI system can be determined with better precision, but errors in the values of C^p that arise as a result of the flow tubing cannot be eliminated.

Equation (15) can be further simplified by setting $t_p = 0$ and $C_{nr}^p = C_r^p$ and by substituting Δt for $(t_{nr} - t_r)$:

$$k = \left(\frac{Q}{V}\right) \frac{(\Delta t)}{(t_r)}. \quad (16)$$

Setting $C_{nr}^p = C_r^p$ requires that the experiment be performed without an injection: this is easily accomplished by completely filling the WST with sample [e.g. Ce(IV) solution] and washing the sample from the WST with reagent (e.g. oxalic acid) or buffer. In this manner only data from the trailing edge of what would be the FI peak is collected and C^p and t_p for the no-reaction experiments are normalised.

Thus, a first-order rate constant can be calculated by measuring the time it takes for the

sample to wash from a WST that is filled with (a) buffer and (b) reagent and by measuring two parameters of the FI system: Q and V . It is interesting to note that in the determination of k by this procedure it is the chemistry that controls the time between events on the x -axis. In this manner the WST FI method is not the flow injection analog of a 'batch' method and is an example of the advantages to be gained in performing chemistry in a flowing stream. Unfortunately, the theoretical basis of the method is a flow system that consists entirely of a well-stirred tank and does not include the more general situation of coiled or knotted mixing devices and loop-injection. This way of determining k should be ideal for teaching laboratory experiment in which the collection of concentration-time data is difficult without adequate spectrophotometers and microprocessors. With a flow cell and a spectrophotometer that has a chart recorder analog output, t_{nr} and t_r can be measured with a ruler from t_p (when the valve is turned) and the rate constant determined to a reasonable degree of precision.

Extension of the model

It is possible to extend the well-stirred model to accommodate other experimental situations such as the monitoring of the product absorbance-time profile and the removal of sample by a second-order (or higher-order) reaction. The equation to describe the product profile can be derived from the equations that describe the sample concentration-time profile for the non-reaction and reaction situations (for the trailing edge of the peak, equations 8 and 9). The absorbance at infinite time can be determined by the same procedure. For higher-order reactions, the derivation of a working equation is complicated because of the imposition of an n th-order removal of sample by reaction on the first-order wash-out. The resulting equation [$a = (Q/V)$],

$$a \left(\frac{C_p}{C} \right)^{n-1} - a e^{a(n-1)t} = k (C_p^{n-1} e^{a(n-1)t} - C_p^{n-1}) \quad (17)$$

requires more data handling to obtain rate constant data ($k = \text{slope}$), but is similar to the experiments described above in that the required concentration-time data can be obtained from a single flow injection experiment.

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