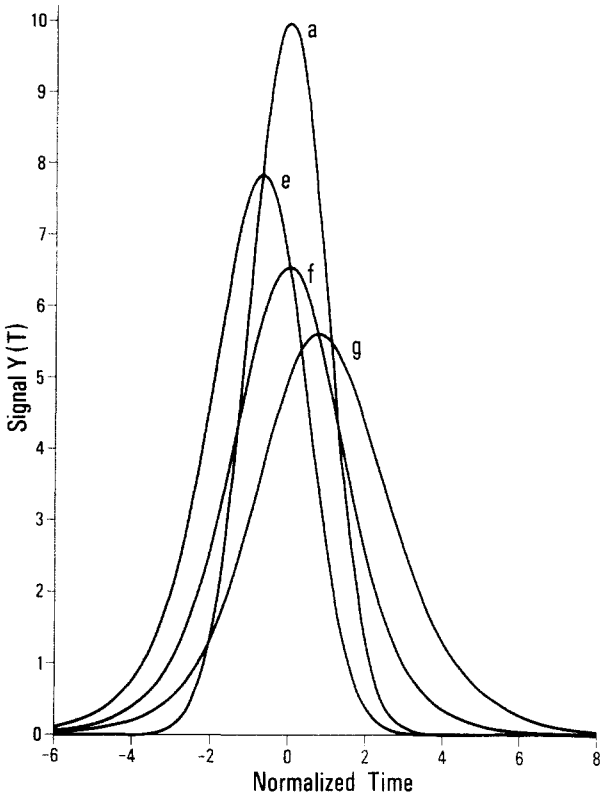

Figure 2. (a) Normalized Gaussian, $\sigma_G = 1$. (e) First-order EMG: $\tau = -1$. (f) Second-order EMG: $\tau_1 = -1$, $\tau_2 = +1$. (g) Third-order EMG: $\tau_1 = -1$, $\tau_2 = \tau_3 = +1$.

EMG function will always intersect the $(n-1)$th order profile.

A special case arises if only two of the time constants coincide, for instance $\tau_2 = \tau_3$. In ref 3 (p 159) $D_1{*}D_2{*}D_2$ is given and we get for the modifying function

$$f(x_1,x_2,x_2) = \frac{1}{\tau_2 - \tau_1}[\tau_2 f(x_2,x_2) - \tau_1 f(x_1,x_2)] \quad (22)$$

FRONTING

Until now we have only considered relaxation times that characterize tailing peaks. To represent fronting peaks, we have to inverse the process and to allow negative τ, as indicated by McWilliam and Bolton (2). Whereas it is easy to find effects with positive time constants, it is more difficult to find effects with negative time constants. (The inverse of exponential decay would be an exponential increasing release from a finite reservoir.) But, as a fact, experimental peaks often manifest fronting that can be fitted with a negative time constant.

To extend the model to fronting, we have to inverse time in eq 7. We introduce formally the sign factor ϵ

$$\epsilon_i = \tau_i/|\tau_i| \quad (23)$$

it is +1 for a positive and −1 for a negative time constant. The generalized argument, eq 5, is

$$x_i = \epsilon_i\left(\frac{\sigma_G}{\tau_i} - T\right) \quad (24)$$

and with this generalized x we have in addition to change eq 7 to

$$p(x_i) = \epsilon_i e^{x_i^2/2}\int_{x_i}^{\infty} e^{-\theta^2/2}\,d\theta \quad (25)$$

Using now the generalized $p(x)$ from eq 25 in eq 8 and 9, we can also manage negative values of τ. With one single negative time constant we get first-order fronting peaks, as curve e of Figure 2. The negative ϵ of eq 25 compensates for the negative sign of S_τ in eq 8 and with the negative ϵ of eq 24 the value of $p(x)$ is altered so that the modifying function $f(x)$ has a value greater than 1 on the leading edge of the peak.

The generalized x and $p(x)$ applied to eq 15 and 19 gives the correct answer for any combination of positive and negative time constants. The derivative, eq 10, is to be altered as follows:

$$\frac{dp(x_i)}{dT} = 1 - \epsilon_i x_i p(x_i) \quad (26)$$

Application of the generalized eq 23 to 26 to the cases of two or three equal time constants gives the correct answer too. Curve f in Figure 2 is an example of a positive and a negative time constant (in the case shown, a symmetrical, non-Gaussian peak); curve g is for one negative and two positive time constants.

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Mechanical Removal of the Central Sample Zone To Avoid Air Bubbles in Monosegmented Continuous Flow Analysis

Célio Pasquini

Instituto de Química, Universidade Estadual de Campinas, 13081 Campinas, São Paulo, Brazil

The method of monosegmented continuous flow analysis (MCFA) was recently introduced (*1*). In this approach the sample is introduced into the system between two air bubbles that avoid large sample dispersion even for long residence times. For this reason, MCFA can operate at high sample throughput even with spectrophotometric determinations that require slow chemical reactions.

In the first paper about MCFA (*1*), the air bubbles were removed by permeation through a PTFE membrane. The system is very simple and works satisfactorily. However, the

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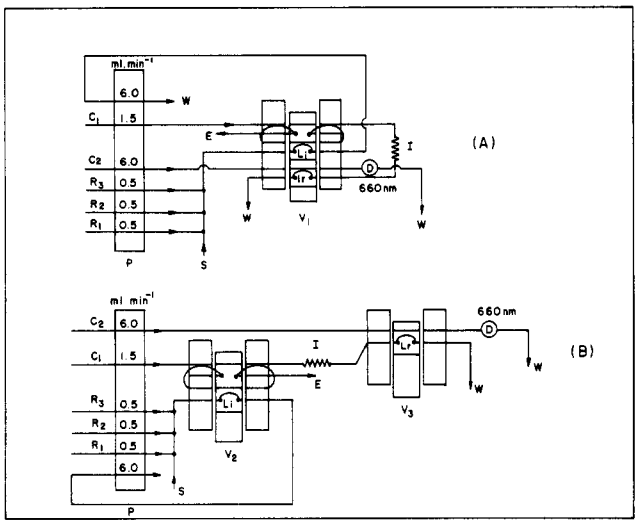

Figure 1. Monosegmented continuous flow analysis manifolds with mechanical removal of central sample zone: A, using only one valve; B, using two valves. Key: P, peristaltic pump; V_1, V_2, and V_3, valves; C_1, carrier stream to incubation coil; C_2, carrier stream to detector; E, to a water aspirator; W, to waste; Li, initial sample loop; Lr, detector sample loop; I, incubation coil; D, detector; S, sample; R_1, R_2, and R_3, reagent streams of sodium hypochlorite, phenol/prussiate, and masking alkaline solution, respectively. Both manifolds are in sampling position.

commercial PTFE tape used lasts only 6–8 h. After this time some small bubbles begin to penetrate into the flow cell, causing imprecise measurements. Further, and more important, this approach suffers from the same kind of limitation observed in other continuous flow systems. The wash time, and thus the analytical rate, is established by the same stream that carries the sample. This seems to be an obstacle to miniaturization of the analyzer since the use of a high carrier flow rate (in order to minimize washing time) requires a larger incubation coil to obtain the desirable sample reaction time. Additionally, much of the washing liquid volume used to reduce the intercontamination to acceptable values is require by the nonsegmented portion existent after the bubbles are removed. This requirement significantly lowers the analytical rate.

In this work a mechanical removal of the central sample zone of MCFA is proposed with the view of substituting the membrane air permeation cell previously used for elimination of air bubbles before detection (*1*). It is also demonstrated how the proposed system can be used both for analyzer miniaturization and for increasing the analysis rate, using the spectrophotometric determination of ammonia as an example.

EXPERIMENTAL SECTION

The fluids were impelled with a peristaltic pump (Ismatec MP 13 GJ4) employing Tygon pumping tubes. The measurements were performed in a photometer, constructed in this laboratory, similar to that previously described (*2*) based on a LED light source (λ_{max} = 660 nm) with a LDR as detector. A flow cell made of acrylic with a 1 cm optical path and about 40 μL total inner volume was used. The signals were registered with a strip chart recorder (ECB, RB 101).

The reagent solutions used for ammonia determination were as follows: R_1, 0.2% (w/v) sodium hypochlorite; R_2, 2% (w/v) phenol and 1% (w/v) sodium prussiate; and R_3, masking solution of 5% (w/v) EDTA and 0.5 M sodium hydroxide. All chemicals were reagent grade except the sodium hypochlorite solution, which was obtained from a commercial bleach. Fresh deionized water was used for all solutions and in the carrier streams.

Figure 1 shows the flow manifolds proposed for mechanical removal of central sample zones from MCFA systems. The air bubble volumes were 25 μL. Both the manifolds work in the same way, removing a fixed volume from the central part of the monosegmented sample at the end of the incubation coil and introducing it into the detector line, while the remainder of the solution and the air bubbles pass to waste. The sample volume originally introduced (Li) was 300 μL and the removed volume (Lr) was 200 μL in both manifolds.

Manifold A uses only one valve operated by means of two solenoids controlled by a single-board microcomputer (Telematic, TSI-1000). With this valve, a new sample is introduced while, simultaneously, a portion of a previously introduced sample, that residing in loop Lr (after the incubation coil), is sent to the detector. The system is programmed so that the segmenting air bubbles are not in loop Lr at the time the valve is moved.

Manifold B employs two valves. One is used for monosegmented sample introduction and is operated automatically as described for manifold A. The other is used to inject an appropriate portion of the liquid into the detector and is operated manually.

The connection of the system to the flow cell was made with a 0.5-nm (i.d.) polyethylene tube 10 cm long in order to avoid undesirable dispersion after sampling the reaction product. The incubation coil I (Figure 1) is made of polyethylene tube (2 mm i.d.) with 150 cm length and wound with 8 cm diameter. Prior mixing of sample and reagents is performed by using six consecutive mixing points constructed as in the literature (*3*). Sample replacement at line S was carried out when the sample valves (V_1 or V_2) were in the injection position.

RESULTS AND DISCUSSION

In MCFA the flow rate (F) that carries the monosegmented sample can be expressed by the equation

$$F = \frac{V_S + V_B + V_W}{t_i + t_a}$$

where V_S (mL) is the sample volume, V_B (mL) is the air bubble sum volume, V_W is the wash liquid volume, t_i (min) is the time necessary to introduce the sample and the two air bubbles into the incubation coil, and t_a (min) is the time required for a new sampling operation when much of the wash fluid is pumped. The analytical rate is determined by the time cycle operation ($t_i + t_a$). The length of incubation coil (L) is defined by

$$L = \frac{tF}{\pi(d/2)^2} \qquad (2)$$

where t (min) is the incubation time interval and d (cm) is the tube diameter.

For a previously defined incubation time, eq 2 shows that a low flow rate is necessary for reduction of the incubation coil length. In the MCFA manifolds described previously (*1*) a typical flow rate of 4 mL·min^{-1} was employed to assure sufficient wash liquid volume with a cycle time of 30 s. For ammonia determination, an incubation coil 3 m long with 2 mm i.d. was necessary.

With the manifolds proposed in this work, a lower flow rate (1.5 mL·min^{-1}) can be employed and the wash volume (V_W) can be reduced because only the segmented part of the analyzer needs to be cleansed. An incubation coil of only 1.50 m, with 2 mm i.d. tube, is then sufficient for obtaining an incubation time of around 210 s. With the reduction of wash volume a increase in analytical rate from 120 to 150 samples per hour was obtained using manifold B (t_i = 16 s and t_a = 8 s). Manifold A operated with a time cycle of t_i = 18 s and t_a = 12 s (allowing 120 samples per hour to be introduced) because syncronism was observed without coil length changes. The reduction of the incubation coil to half its length and the increase in analytical rates demonstrate the advantages of working with incubation times and wash times defined by two independent flow rates in MCFA.

A comparison between the two manifolds proposed here reveals that manifold A is actually simplier than manifold B although it is more difficult to define the necessary synchronous operation when the manifold is first employed. Further, it may be very difficult to connect the valve to the detector in minimum volume when a large detection instru-

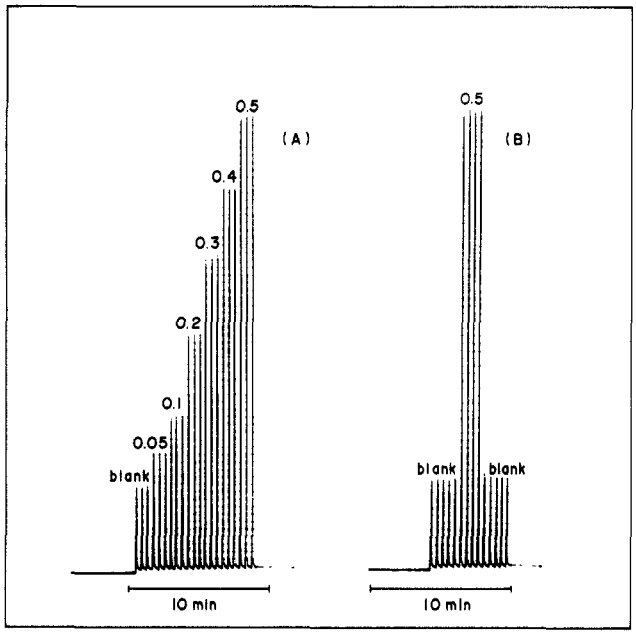

Figure 2. (A) calibration run for ammonia determination with manifold B. The numbers over the peaks are the ammonia concentrations in $\mu g \cdot mL^{-1}$. All measurements were made in triplicate. (B) Signals obtained using the same manifold after 2 h showing the stability and absence of carry-over between blanks and 0.5 $\mu g \cdot mL^{-1}$ ammonia standard solution.

ment is used. On the other hand, the second valve of manifold B (V_3) can easily be placed near the detector and there are no difficulties with synchronism. Additionally, the operation of manifold B can be fully automated by automating the second valve operation. This can be achieved by using a circuit that can detect air bubbles, as previously described (*4*).

Ammonia determinations were made with both manifolds. With the LED/LDR colorimeter a calibration curve linear through 0.7 $\mu g \cdot mL^{-1}$ with a correlation coefficient of 0.9996 was obtained. A detection limit of 5 $ng \cdot mL^{-1}$ was estimated from the blank standard deviation measurements at 99% confidence. Reproducibility is better than 1% and a negligible carry-over exists between samples, as shown in Figure 2.

Another aspect of the system proposed in this work is that it can effectively provide for coupling the technique of MCFA with that of FIA. One application could be when the chemistry required for a determination envolves a slow reaction followed by a rapid one. In this case, the slow reaction would proceed in a MCFA manifold (taking advantage of its low sample dispersion for long residence time) while the second reaction could take place with the resampled volume by introducing it in a carrier reagent fluid (single-line FIA manifold) or in an inert carrier fluid that merges with the reagent, passing through an incubation coil and then through the flow cell.

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Multifunction Valve for Flow Injection Analysis

Jun-ichi Toei* and Nobuyuki Baba

Development Department, Scientific Instrument Division, Toyo Soda Manufacturing Company, Ltd., 2743-1 Hayakawa, Ayase-shi, Kanagawa 252, Japan

The reproducible introduction of a precisely measured volume of sample into a moving carrier or reagent stream is one of the basic factors that must be fulfilled in order to ensure the successful performance of any flow injection analysis (FIA) system (*1*, *2*). Numerous devices for introduction of samples have been proposed (*3*–*5*) and now hexagonal valves such as the Rheodyne 7125 are popular for the purpose. Though they have brought precise introduction of samples, the trouble is that they have only that function. As Ruzicka had already pointed out, a parallel introduction of sample and reagent is very important in FIA. Mindegaard and Bergamin have proposed injectors that have those two functions (*6*, *7*). They have reduced consumption of expensive reagents and obtained good success with the valves. But they still have a disadvantage in that introduction of samples could not be performed without a separate operation.

In a previous paper (*8*) we have reported a new-type valve by which sample injection and flow change-over of a stream could be performed at the same time. Now we have designed and fabricated a simple and new type of injector that has two functions, that is, introduction of sample or sample and reagent (*9*).

EXPERIMENTAL SECTION

Injector. Figure 1 shows the cross sectional view of the injector, in which 1 is a stator of a circular plate shape and 2 is a rotor. The rotor is made of Teflon and the stator is made of Kel-F which is surrounded by a stainless steel frame in order to stand the high pressure. This valve can operate satisfactorily under 50 kg/cm^2. This valve has three positions and we can select each position with ease by use of a pulse motor that makes the rotor rotate clockwise or counterclockwise. The precise positioning can be performed by use of photosensors as a position indicator. Figure 2 shows the shapes on the surface of the stator and the rotor. The small openings a to j and the grooves a′, a″, a‴, f′, f″, and f‴ are at the stator and the grooves A to G are at the rotor. In the stator the small opening a is connected to a pump and f is connected to reaction tubing. The small openings b,e and g,j are connected to a sample and a reagent loop, respectively. The small openings c,d and h,i are also connected to a circuit of sample and reagent charge.

Arrangement. Figure 3 shows the arrangements of the flow formed by the stator and the rotor, (a) is the load position, (b) is the sample injection position, and (c) is the reagent and sample injection position (after this we call the position "reagent injection position"). In load position, a solution flows f–F‴–A–a‴–a and a sample and a reagent are charged into the loops, respectively.

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