

# Extending On-line Dilution Steady-state Concentration Range by Modification of the Merging Stream and Tandem Injection Continuous-flow Methods

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The range of steady-state concentrations, which had been achieved previously by on-line dilution constant-flow methods including flow injection, has been extended by the introduction of new flow configurations. The extent of dilution achieved depends on their combined arrangement. The replacement of constant-flow channels by either completely or partially variable flow channels has extended the dilution range. Moreover, a flexible flow approach for on-line dilution is also achieved. With a totally variable speed flow, an on-line dilution system can be operated at a constant over-all flow-rate over all of the achievable dilutions. Hence the precision of the steady-state concentration section is improved, as the choice of a single efficient coil or coil assembly becomes possible. The most effective means of extending the dilution range is stream flow splitting of the diluted sample produced by the merging stream or tandem injection approach followed by remerging the split stream with the diluent. This combination can in practice provide any desired dilution irrespective of whether constant or partially variable speed flow is adopted. On-line dilution of more than 300 000 is demonstrated. Hydrodynamic injection was as effective in performing tandem injection on-line dilution as conventional tandem injection and yielded identical precision of the steady-state concentration. Each of these dilution techniques can be treated as a module with specific dilution features which can be combined with each other to provide specific steady-state concentration on-line dilution.

**Keywords:** *Tandem injection and hydrodynamic tandem injection; merging stream; on-line dilution; stream flow splitting and remerging; inductively coupled plasma atomic emission spectrometry*

Israel *et al.*<sup>1</sup> recently developed on-line dilution methods with steady-state concentrations by exploiting continuous-flow configurations including flow injection (FI). Israel and Barnes<sup>2</sup> applied these on-line dilution methods to sequential, multi-element analysis of soil sample digests with inductively coupled plasma atomic emission spectrometry (ICP-AES).

The basic requirement of these methods is to produce on-line dilutions with reproducible steady-state concentrations for both standard and sample solutions. For these conditions the precision and accuracy of the results depend solely on sample preparation and detector measurements. The expected on-line dilution at pre-set conditions can be calculated from derived relationships.<sup>1,2</sup> As the sample and standard solutions in any determination series undergo identical dilution, knowledge of the exact dilution has no consequence on the precision and accuracy of the results. The steady-state concentration on-line dilution approach is especially suited for operation with sequential detectors when multi-component determinations are sought, because these determinations require a finite measurement time. Therefore, these determinations can be implemented only with steady-state concentration dilutions.

In addition to increasing the speed of analyses, on-line dilution reduces the dangers of handling hazardous materials and permits in-line conditioning of the diluted sample (*i.e.*, adding acids, bases or buffers to adjust the pH; salts to maintain the ionic strength; and reagents to produce chemically active specific detectors, or to improve the accuracy of the results by either the addition of an internal reference standard or by performing standard additions). These operations can be performed simultaneously with on-line dilution, and they contribute to the reproducibility and flexibility of analytical determinations.

The dilution factors realized by the merging stream principle are limited and depend on the total stream to sample

flow-rate ratios. In this approach, the sample solution is merged with the diluent in a single (Fig. 1) or double confluence (Fig. 2) junction(s). Efficient mixing coils are employed, which must have dimensions matched to the over-all flow-rate to the detector. In addition, a flow-rate interfacing device for the on-line manifold and the detector is important.<sup>1,2</sup>

The merging stream configurations do not require time-based control devices and are usually simple to construct. For this reason the merging stream principle is very attractive. An early example with FI was described by van Staden.<sup>3</sup> The prospect of extending its dilution capabilities is tempting, and two approaches are examined here to facilitate expanded on-line dilution.

The use of a variable- instead of a constant-speed peristaltic pump was suggested previously to simplify merging-stream manifold manipulations and to implement the design of a laboratory-built manifold module which can produce all possible dilutions without any alterations.<sup>2</sup> Often, FI systems employ a fixed-speed pump and require that the pump tubing diameter be changed to alter the stream flow-rate. Generally, a variable-speed pump is capable of attaining higher dilutions than a constant-speed pump.

For a constant-speed peristaltic pump operating with a flow manifold of constant dimensions including the mixing coil(s), the residence time of the sample-diluent mixture between each confluence junction and the detector will vary according to the over-all flow-rate. Conceivably, an efficient mixing coil for a certain over-all flow-rate range can become less effective when the flow-rate exceeds this range. The precision of the steady-state concentration section will deteriorate owing to the low residence time, which requires the use of a more efficient coil assembly. Further, excessive flow-rates generate high back-pressure. These considerations limit the applicable flow-rate and the extent of dilution. The flow-rate ratio of the diluent to sample must also be considered.

In order to minimize some of these limitations, a variable-speed peristaltic pump is employed. Hence, the over-all

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flow-rate can be maintained constant by operating the variable-speed pump motor at some controlled fraction of its maximum. This facilitates an increase in the dilution limit by increasing the diluent to sample flow-rate ratio. The consequence of operating at a constant over-all flow-rate is that an efficient mixing coil for one dilution is efficient for all dilutions, as the residence time is the same. Therefore, the precision of the steady-state concentration is uniform for all dilutions.

In order to extend the dilution limit significantly the most promising approach usually is to split a small volume fraction of the sample–diluent mixed stream and to remerge it typically with a large volume ratio of the diluent (*i.e.*, cascade dilution). The flow-rate ratio at reemergence of the diluent with the diluted sample is high in order to effect a secondary high dilution with this stream flow splitting and reemerging (SFS-RM) step. This approach was suggested previously<sup>1</sup> and was simultaneously employed by Whitman and Christian<sup>4</sup> for FI applications that produced transient concentration profiles.

The SFS-RM device is illustrated in Fig. 3, in which a T-junction and two peristaltic pump channels are needed to carry out this operation. The resulting dilution factor of this proposed technique is equal to the product of the dilution factors of the consecutive merging operations. If the SFS-RM step is repeated, any desired dilution can be achieved conceptually. When SFS-RM is also combined with a variable-speed flow or a combination of a constant- and variable-speed flow, a wide range of dilutions can be produced.

Stream splitting has been suggested for various FI applications.<sup>4–10</sup> Basson and van Staden<sup>5</sup> applied stream splitting alone for the simultaneous determination of Na, K, Ca and Mg with a flame photometer. Fernandez *et al.*<sup>6</sup> used stream splitting for the simultaneous determination of a specific analyte under various dispersion conditions and suggested that the approach could be adapted for differential kinetic analysis. Mindel and Karlberg,<sup>7</sup> Whitman and Christian,<sup>4</sup> and Clark *et al.*<sup>8</sup> applied the split zone technique in a sample pre-treatment system with much the same arrangement as suggested here. In effect, SFS-RM is analogous to FI dilution by the re-injection of the split sample zone.<sup>9,10</sup> However, re-injection of a split sample yields transient concentration profiles and requires the use of an additional valve synchronized with the conventional FI valve.

A novel approach was adopted earlier, employing tandem injection.<sup>1</sup> A discrete sample volume,  $V_i$ , was injected in tandem into a continuously flowing diluent stream. In order to obtain adequate precision of the resulting steady-state concentration section, the injection cycle volume was the sum of  $V_i$  and the cycle diluent volume,  $V_D$ .<sup>1</sup> However,  $V_D$  must not be unduly extended. In addition, the flow manifold must be designed for medium to high dispersion conditions. Diverse dilutions can then be achieved to produce steady-state concentrations by varying  $V_i$  and  $V_D$ . The dilution factor achieved by tandem injection is dependent on the volume ratio of the injection cycle to the sample injection. With time-based FI equipment, substituting times  $t_i$  and  $t_D$  instead of  $V_i$  and  $V_D$ , respectively, is appropriate, as the sample injection in a plug form conventionally is affected by the diluent flow.

In practice, only a combination of tandem injection with merging stream was applied to steady-state concentration on-line dilutions in order to avoid temporal concentration ripples.<sup>1</sup> The resulting dilution factor is, therefore, the product of the dilution factors achieved with each of the independent methods. Henceforth, in this paper, 'tandem injection' will refer to the combination of both methods.<sup>2</sup>

Růžička and Hansen<sup>11,12</sup> introduced hydrodynamic injection, which involves intermittently operated dual pumps. Unlike FI equipment, no moving parts are involved, but time-based equipment is required to synchronize the operation of the pumps. In the conventional FI time-based operation, only a single valve is necessary. One important

feature of hydrodynamic injection is that it permits a considerable saving of sample volume. With tandem injection, sample economy is pronounced especially when the ratio of the tandem injection cycle period to the injection time ( $t_{TI}/t_i$ ) is high.<sup>1</sup> For both methods the sample must fill the dead volume. However with hydrodynamic injection the sample flow stops as the diluent flow starts.

The use of hydrodynamic injection for tandem injection on-line applications offers an additional incentive in sample conservation. No sample loop must be filled repeatedly. However, the flow manifold for 'hydrodynamic tandem injection' contains more T-junctions than are needed for conventional tandem injection. Otherwise, the use of hydrodynamic tandem injection instead of conventional tandem injection for steady-state concentration on-line dilution is expected to yield identical results.

The same modifications which are examined here for extending the merging stream on-line dilution range can also be applied to tandem injection or hydrodynamic injection. The use of a variable- instead of a constant-speed peristaltic pump promises to extend the upper dilution limit achievable with a constant-speed pump. A considerable simplification of the flow manifold for both methods can result. Stream flow splitting and reemerging is expected to improve the tandem injection approach as with the merging stream method, *i.e.*, to extend the dilution limit significantly. However, the application of a single SFS-RM module to hydrodynamic tandem injection would require additional T-junctions compared with the same manifold operated in the absence of SFS-RM. This complicates the flow manifold design and can make its operation difficult.

The purpose of this study was to examine the feasibility of applying hydrodynamic injection for use as a tandem injection device in order to conserve sample. The utility and advantages of replacing a constant- by a variable-speed peristaltic pump were also studied for the merging stream and tandem injection steady-state on-line dilution configurations. In addition, the feasibility of applying SFS-RM and its combination with a variable-speed peristaltic pump or with constant- and variable-speed pumps was examined for all the on-line dilution steady-state concentration methods. These experiments were performed mainly to extend the dilution range and to eliminate unnecessary sample manipulations. In this study, the application of hydrodynamic tandem injection is the only modification that does not aim at extending the dilution range.

## Experimental

### Flow Manifolds for Merging Stream Dilution

A four-channel, variable-speed peristaltic pump,  $P_1$  (Rainin Rabbit), coupled with three different flow manifolds was used for each of the merging stream on-line dilution configurations (Figs. 1–3). Laboratory-built flow modules were prepared for each application, and each was connected to the peristaltic pump tubes on one side and to the nebulizer peristaltic pump,  $P_2$ , of an ICP-AES detector on the other. Y-Connectors were used for confluence junctions, and T-connectors for both the SFS and the SFS-RM devices. The first serves as a flow-rate interface between the flow manifold and the ICP-AES detector.<sup>1,2</sup> Both  $P_1$  and  $P_2$  were operated simultaneously, and the diluted sample total flow-rate was always maintained in excess of the optimum nebulizer flow-rate. Therefore, SFS is necessary to divert to waste (W) the excess of diluted sample that does not flow through  $P_2$ .

Two channels of  $P_1$  were employed for the sample (S) and diluent ( $D_1$ ) streams followed by mixing in an efficient coil (a) for the single confluence junction illustrated in Fig. 1. An additional channel of  $P_1$  was required to achieve a second confluence junction with the diluent ( $D_2$ ) followed by mixing in two additional coils (b and c) as illustrated in Fig. 2. For the

SFS-RM flow manifold illustrated in Fig. 3, four channels of  $P_1$  were utilized. Two channels were used for a single confluence merging of the sample with the diluent. One channel was employed to withdraw a fraction of the diluted sample through  $P_1$  at a usually low flow-rate to be remerged with a fourth channel of the diluent ( $D_2$ ) through  $P_1$  at a usually high flow-rate ratio of the diluent to the split diluted sample. Flow module tubing [Fisherbrand Accu-Rated poly(vinyl chloride)] was used, and the flow-rates in the peristaltic pump tubing were measured at 100% of the pump motor speed to allow the calculation of the expected dilutions.<sup>1,2</sup>

In order to calculate accurately the anticipated dilutions from the flow-rates, the flow-rate in each tube must be determined repeatedly and the mean values used. Tubing with the same nominal dimensions can produce different flow-rates. These measurements must also be carried out at the same motor speed and at about the same time as the on-line dilution operations. Also, the flow-rate continuously changes as the tubing fatigues, and the fraction of the pump motor speed does not yield precisely the same flow-rate fraction. As these considerations were not implemented in this study, the flow-rate values indicated must be considered to be approximate and serve only for rough evaluation of the expected dilutions.

Experimental dilutions were usually determined from intensity measurements at the maximum Sc II 361.384 nm emission.<sup>1</sup> The total flow-rate of the diluted sample at 100% motor speed was able to exceed  $1 \text{ ml min}^{-1}$ , the flow-rate used for  $P_2$ . However, if it exceeded  $2.0 \text{ ml min}^{-1}$ , the motor speed

was decreased accordingly to keep the flow-rate to below  $2.0 \text{ ml min}^{-1}$ .

This arrangement is advantageous in facilitating the selection of an effective mixing coil assembly for each configuration.

### Flow Manifolds for Tandem Injection Dilution

Three types of tandem injection flow manifold were adopted for the following applications: conventional with a combination of a constant- and a variable-speed peristaltic pump; hydrodynamic with a constant-speed peristaltic pump; and conventional with SFS-RM modification with either a constant- or a combination of constant- and variable-speed peristaltic pumps.

A commercial FI instrument (Tecator FIAstar 5020 analyser) with a four-channel, constant-speed peristaltic pump was used for all these tandem injection configurations.<sup>2,13</sup> However, a four-channel, variable-speed peristaltic pump (Rainin Rabbit) was coupled with the operation of the FI instrument, when variable-speed flow channels were partially used for conventional injection with or without an SFS-RM device.

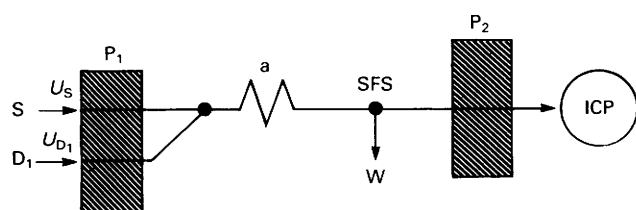
Replicate determinations at the steady-state section of on-line dilutions were performed following the same procedures as applied previously.<sup>1</sup> However, both scandium and lanthanum were used for intensity measurements at Sc II 361.384 nm and La II 379.478 nm lines.

### Conventional Tandem Injection Configuration With a Variable-speed Peristaltic Pump

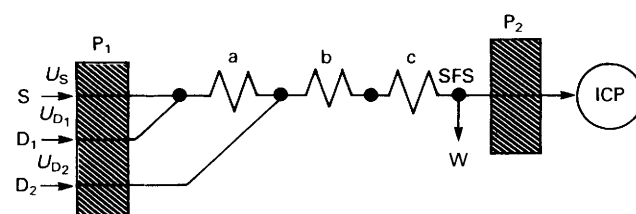
The flow configuration, illustrated in Fig. 4, is essentially identical with the previously described flow arrangement<sup>1</sup> except that a single instead of a double confluence, a variable-speed pump for the diluent channel ( $D_1$ ) and minor coil assembly modifications were made.

### Hydrodynamic Tandem Injection With Dual Constant-speed Peristaltic Pumps

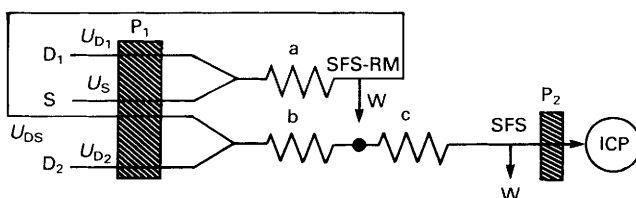
The conventional tandem injection configuration can be reproduced by the application of an intermittent pumping configuration illustrated schematically in Fig. 5. A time-based control device (T) was programmed to operate the dual constant-speed pumps ( $P_1$  and  $P_2$ ) in an intermittent stopped-flow mode. The pump,  $P_1$  was operated for a period of time  $t_1$ , while  $P_2$  was stopped for the same period of time, and *vice versa*, for a period of time,  $t_2$ . This cycle was repeated at will by programming the timer, T. During the time period



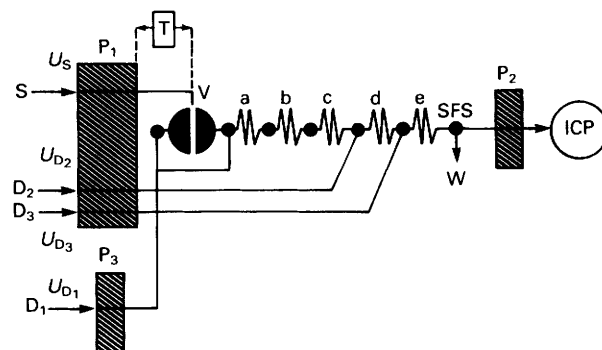
**Fig. 1** Schematic diagram of a single merging stream on-line dilution configuration:  $P_1$ , four-channel variable-speed peristaltic pump;  $P_2$ , peristaltic pump of the ICP-AES detector (ICP) with a flow-rate of approximately  $1.0 \text{ ml min}^{-1}$ ; SFS, interfacing stream flow splitting T-junction; W, waste and a, coil (length in cm/i.d. in mm) 40/1.42. Flow-rates,  $U$ , in  $\text{ml min}^{-1}$ ;  $U_S$  and  $U_D$  are the sample and diluent, respectively (cf. Table 1)



**Fig. 2** Schematic diagram of a double merging stream on-line dilution configuration: flow-rates,  $U$ , in  $\text{ml min}^{-1}$ ;  $U_{D1}$  and  $U_{D2}$ , first and second diluent merging streams, respectively (cf. Table 1). Coils: b, 41/0.75; and c, 41/1.42. Other notations as in Fig. 1



**Fig. 3** Schematic diagram of a single merging stream, stream flow splitting (SFS-RM) on-line dilution configuration:  $U_{DS}$ , flow-rate on splitting of the diluted sample (cf. Table 2). Other notations as in Fig. 2



**Fig. 4** Schematic diagram of tandem injection on-line dilution with double merging stream and a variable-speed flow through the diluent ( $D_1$ ).  $P_1$  and  $P_2$ , pumps (cf. Fig. 1);  $P_3$ , variable-speed peristaltic pump; T, timer; and V, injection valve. Flow-rates in  $\text{ml min}^{-1}$ :  $U_S$ , 1.21; and  $U_{D1}$ , 0.32 (at 100% motor speed). Three flow configurations were used: a,  $U_{D2}$  and  $U_{D3}$ , 0.65; b,  $U_{D3}$ , 1.21; and  $U_{D3}$ , 2.42; c,  $U_{D2}$  and  $U_{D3}$ , 2.42. Coils: a, 40/1.42; b, 50/0.7; c, 40/1.0; d, 50/0.7; and e, 40/1.42

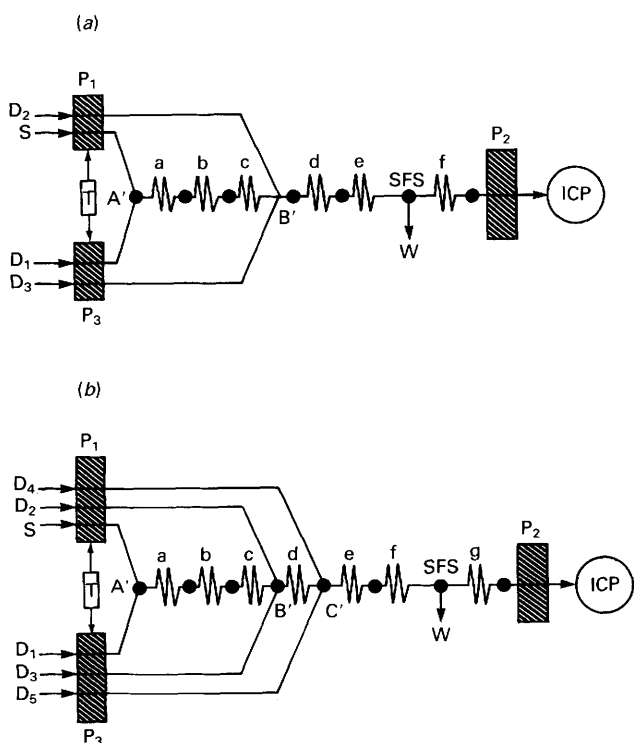


$t_1$ , the sample (S) and the diluent streams [ $D_2$  in Fig. 5(a) or  $D_2$  and  $D_4$  in Fig. 5(b)] flow continuously through the respective channels, while the diluent streams [ $D_1$  and  $D_3$  in Fig. 5(a) or  $D_1$ ,  $D_3$  and  $D_5$  in Fig. 5(b)] are idle. However, during time period  $t_2$  the sample (S) and the diluents ( $D_2$ , or  $D_2$  and  $D_4$ ) are idle, while the diluent streams ( $D_1$  and  $D_3$ , or  $D_1$ ,  $D_3$  and  $D_5$ ) flow continuously through the respective channels. This intermittent flow is repeated a pre-set number of times. As soon as the sample crosses junction A', one sample zone after another will be sandwiched between the diluent zones, thus triggering dispersion between adjacent layers. This pattern is identical with that which occurs in the tandem injection approach.<sup>1</sup> A flow-rate interfacing SFS junction was inserted for every configuration. Tandem hydrodynamic injection with a variable-speed peristaltic pump was not attempted owing to the absence of suitable equipment.

The sample channel S is designed to be as short as possible in order to confine the dead volume before reaching the confluence junction A'. As described above, the sample flow stops during time period  $t_2$  in contrast to conventional tandem injection operation wherein the sample continues to flow to the valve loop to waste or directly to waste during both the run and injection periods. Hence, a considerable saving in sample volume results when intermittent pumping is employed for steady-state concentration on-line dilution. When the ratio  $t_2:t_1$  is high, the sample volume is a minimum. A preliminary study to apply SFS-RM to hydrodynamic injection using constant-speed peristaltic pumps was carried out; however, the high back-pressure created hindered regular manifold operation.

#### Tandem Injection Dilution With SFS-RM Device With Constant- and Variable-speed Peristaltic Pump Operation

Tandem injection was examined using a single confluence with the diluent prior to SFS-RM. Five channels were devoted to



**Fig. 5** Schematic diagram of hydrodynamic tandem injection on-line dilution using intermittent pumping, with (a) single- and (b) double-confluence stream junction(s) A', B' and C'. P<sub>1</sub> and P<sub>2</sub>, dual four-channel constant-speed peristaltic pumps operating in the intermittent pumping mode. Coil f, 40/1.0. Flow-rates (in ml min<sup>-1</sup>):  $U_S$ , 1.21;  $U_{D1}$ , 0.21, 0.34 or 0.45;  $U_{D2}$ , 1.21 or 2.41;  $U_{D3}$ , 1.21, 2.41 or 3.71;  $U_{D4}$  and  $U_{D5}$ , 2.41 or 3.71. Other notations as in Fig. 4

the sample and diluent streams as illustrated in Fig. 6. The variable-speed peristaltic pump P<sub>3</sub> was utilized to drive the diluent channel D<sub>1</sub> and the diluted sample stream split, while the constant-speed peristaltic pump of the FI instrument was used for driving the sample S and the diluent channels D<sub>2</sub> and D<sub>3</sub>.

#### ICP-AES Detector

A sequential ICP-AES system (Perkin-Elmer Plasma II) with the same operating conditions described previously was employed.<sup>2</sup>

#### Solutions

A stock standard solution of Sc (1000 mg l<sup>-1</sup>) was prepared in 5% v/v nitric acid, as described previously.<sup>1,2</sup> A stock solution of 8000 mg l<sup>-1</sup> of La in 5% v/v nitric acid was also prepared by the dissolution of 6.235 g of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in 250 ml of 5% v/v nitric acid. Various dilutions of both stock solutions were made as necessary.

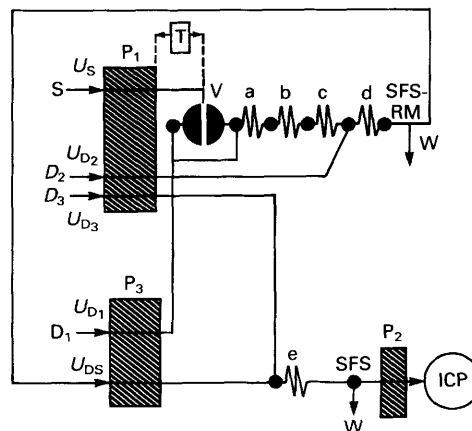
#### Results and Discussion

The procedures applied previously to establish the dilution factor and the precision of the steady-state section using replicate determinations<sup>1</sup> were employed in this study. The results obtained for each of the arrangements are discussed in the following sections.

#### Dilution by Single and Double Confluence Junction(s) With a Variable-speed Peristaltic Pump

The flow systems illustrated in Figs. 1 and 2 were employed for examination of the single- and double-merging stream configurations, respectively. The results obtained are listed in Table 1. The various flow-rates employed resulted in dilutions in the range 1.33–42. The relative standard deviations (RSDs) obtained (0.6–1.3%) are satisfactory, and no significant difference exists compared to the precision of replicate determinations of directly nebulized, pre-diluted standard solutions.

The upper dilution limit obtained by using the double-confluence junction configuration (Fig. 2) was only slightly higher than the corresponding dilution obtained with the single-confluence junction. Therefore, a single merging stream was adopted for other modifications whenever some or all of the channels were operated with a variable-speed pump.



**Fig. 6** Schematic diagram of tandem injection on-line dilution with a single confluence junction, followed by SFS-RM, and a combination of constant- and variable-speed flow channels. All notations as in Fig. 4

The ability to attain these dilutions for a single merging stream is due to the application of a variable-speed pump. Under these conditions, the flow manifold module was considerably simplified. The maximum dilution reported in previous work employing two confluence junctions of the sample with the diluent and a constant-speed peristaltic pump was approximately 15.<sup>1</sup>

One configuration that was not studied combines two peristaltic pumps, at least one of which has a variable speed, and is believed to be more flexible and might deliver slightly higher dilutions. This might be achieved by utilizing a variable-speed pump for driving the sample channel while the diluent channels are driven by either a constant- or a variable-speed pump.

### Single-confluence Junction Dilution, Splitting the Diluted Sample and Remerging, With a Variable-speed Peristaltic Pump

With the flow configuration illustrated in Fig. 3, the results obtained for the single-confluence junction dilution, splitting the diluted sample and remerging, with a variable-speed peristaltic pump are listed in Table 2. Only a few flow-rate combinations of the flow channels were examined to demonstrate high dilutions. Both intermediate and low dilutions are possible with this configuration.

The range of dilutions investigated was approximately 400–2500 with signal precision of 0.73–1.1%. These RSD values are essentially the same as the precision obtained by direct aspiration of the pre-diluted samples. The signal reproducibility achieved with a variable-speed peristaltic pump was uniform for all dilutions. Repeated experiments shown in Table 2 yield satisfactory results and indicate the reliability of using this steady-state concentration on-line dilution method for performing a series of determinations at the same flow configuration. The application of SFS-RM has proved to be a powerful tool for extending the dilution range by almost 50-fold.

**Table 1** Single and double merging stream on-line dilution using a variable-speed peristaltic pump (*cf.* Figs. 1 and 2). Single and double merging stream configurations using a variable-speed peristaltic pump to keep the overall flow-rate at less than 2 ml min<sup>-1</sup> by varying the motor speed. The mean flow-rates are  $U_S$  (sample) and  $U_{D1}$  and  $U_{D2}$  (the first and second diluent merging streams, respectively). The flow-rates used for each experiment are quoted at 100% motor speed. Twenty replicate intensity measurements of Sc II 361.384 nm were made<sup>†</sup> either at the steady-state concentration section for each on-line dilution experiment or for the direct aspiration of a pre-diluted sample

Mean flow-rates*			Motor speed <sup>†</sup> (%)	Dilution <sup>‡</sup> (found)	RSD <sup>§</sup> (%)
$U_S$	$U_{D1}$	$U_{D2}$			
1.41	1.25	—	50	1.87	0.83
1.25	1.41	—	50	2.12	0.99
0.457	1.41	—	75	4.27	0.62
1.41	0.457	—	75	1.33	0.90
0.457	2.28	—	50	5.45	0.93
0.457	4.14	—	30	9.44	0.92
0.457	7.75	—	18	16.8	1.3
0.20	2.28	—	60	12.0	0.85
0.20	7.75	—	20	39.8	1.3
0.20	2.28	4.14¶	25	34.2	1.0
0.20	4.14	4.14¶	20	42	1.1

\* Flow-rates are given in ml min<sup>-1</sup> at 100% motor speed. The actual flow-rate is the product of the quoted flow-rate and the motor speed divided by 100.

<sup>†</sup> Time delay to reach steady-state concentration is 3–4 min.

<sup>‡</sup> Mean value of 20 replicate measurements.

<sup>§</sup> Relative standard deviation of 20 replicate measurements.

¶ Double confluence junction configuration.

### Conventional Tandem Injection With Double-confluence Junctions

Conventional tandem injection with double-confluence junctions operated by a combination of constant- and variable-speed peristaltic pumps is illustrated in Fig. 4. Operation of tandem injection is similar to a previous study.<sup>1</sup> However, the diluent  $D_1$  flows in a variable-speed channel, which enables the dilution to be increased by simply lowering the flow-rate. The results are listed in Table 3 and demonstrate satisfactory precision for a dilution range of 65–2400.

The increase in the upper dilution limit was facilitated by the use of a variable-speed channel for  $D_1$ . The main effect of the application of fractional motor speed to this channel in particular is to enhance the dilution limit. However, the time delay in achieving the steady-state concentration section is dependent on the flow-rate of channel  $D_1$  in particular. The time delay to obtain the steady-state concentration at 20% motor speed is about 20 min. In order to limit this time delay, one of the three coils (*i.e.*, coil c) used for the tandem injection section can be removed without influencing the efficiency of mixing, because the flow-rate of channel  $D_1$  in this example is very low.

### Hydrodynamic Tandem Injection

Hydrodynamic injection on-line dilution operating dual constant-speed peristaltic pumps with intermittent pumping and using a single- [Fig. 5(a)] and double- [Fig. 5(b)] confluence junction(s) was demonstrated with tandem injection on-line dilution for a range of dilutions up to about 900 (Table 4) with similar results to those obtained previously for tandem injection.<sup>1</sup> The only advantage of hydrodynamic tandem injection over conventional tandem injection is conservation of the sample volume.

### Tandem Injection

Results for tandem injection on-line dilution with a single merging stream, followed by SFS-RM using constant-speed flow channels are given in Table 5. Data for variable-speed flow for a number of channels are summarized in Table 6. Operation of this flow configuration is identical with the operation of tandem injection shown in Fig. 4. However, in practice the dilution capabilities of these arrangements handle

**Table 2** Single merging stream coupled with SFS-RM using a variable-speed peristaltic pump (*cf.* Fig. 3). A single-confluence junction of the sample and the diluent followed by SFS of the diluted sample (DS) and remerging using a variable-speed peristaltic pump.  $\dot{U}_{DS}$ , Flow-rate of the diluted sample from the first confluence

Mean flow-rate*				Motor speed <sup>†</sup> (%)	Dilution <sup>‡</sup> (found)	RSD <sup>§</sup> (%)
$U_S$	$U_{D1}$	$U_{DS}$	$U_{D2}$			
0.20	7.75	0.46	4.14	40	432	0.79
0.20	7.75	0.46	4.14	35	425	0.93
0.20	7.75	0.46	4.14	45	435	0.73
0.20	7.75	0.46	7.75	45	884	0.91
0.20	7.75	0.46	7.75	35	848	1.06
0.20	7.75	0.20	4.14	45	873	0.91
0.20	7.75	0.20	7.75	25	2525	1.02
0.20	7.75	0.20	7.75	25	2527	0.80

\* Flow-rates are given in ml min<sup>-1</sup> at 100% motor speed. The actual flow-rate is the product of the quoted flow-rate and the motor speed divided by 100.

<sup>†</sup> Time delay to reach steady-state concentration is 3–4 min.

<sup>‡</sup> Mean value of 20 replicate measurements.

<sup>§</sup> Relative standard deviation of 20 replicate measurements.

any required dilution, even when a constant-speed peristaltic pump is used (Table 5). Dilutions as high as 23000 were realized with the constant-speed peristaltic pump. Very high dilutions of about 300000 were attained with variable-speed flow channels used for the diluent  $D_1$  and the diluted split sample. The influence of using a variable-speed pump for these two channels is significant for extending the maximum attainable dilution. However, achievement of the steady-state concentration is compromised by the resulting time delay in the absence of SFS-RM. This delay is reduced considerably if only the diluted and split sample channel flow is variable. For this arrangement the maximum attainable dilution is about 70000.

**Table 3** Conventional tandem injection on-line dilution with a double-confluence junction and partially variable speed channels (cf. Fig. 4). Dilution of the sample by tandem injection with a double merging with the diluent; the constant-speed peristaltic pump  $P_1$  drives the sample  $S$  and the diluent  $D_2$  streams. Only the diluent  $D_1$  stream is driven by the variable-speed peristaltic pump, and the per cent. motor speed refers only to the last channel

Flow configuration*	Injection time/s	Injection period/s	Motor speed† (%)	Dilution‡ (found)	RSD§ (%)
a	2	25	100	65	1.3
a	2	25	50	128	1.0
a	2	25	30	218	0.9
a	1	25	100	125	1.5
a	1	25	50	255	1.2
a	1	25	30	435	1.1
a	1	30	100	145	1.8
a	1	30	50	297	1.3
a	1	30	30	530	1.3
b	2	25	100	140	1.1
b	2	25	50	290	1.0
b	2	25	30	480	1.1
b	1	25	100	268	1.8
b	1	25	50	595	1.2
b	1	25	30	920	0.9
c	2	25	100	206	2.2
c	1	25	100	414	1.9
c	1	25	50	805	1.3
c	1	25	25	1620	0.7
c	1	30	20	2410	1.1

\* Flow-rates of the various channels: a,  $U_{D_2}$  and  $U_{D_3}$ , 0.65; b,  $U_{D_2}$ , 1.21; and  $U_{D_3}$ , 2.42; c,  $U_{D_2}$  and  $U_{D_3}$ , 2.42 ml min<sup>-1</sup>. Pump tubing diameters given in Fig. 4.

† Time delay to reach steady-state concentration is approximately 6 min at 100%, 12 min at 50% and 20 min at 25% motor speed.

‡ Mean value of 20 replicate measurements.

§ Relative standard deviation of 20 replicate measurements.

**Table 4** Hydrodynamic tandem injection on-line dilution of the sample with a single- and double-confluence junction with the diluent with constant-speed operation. Time delay to reach steady-state concentration is approximately 5–6 min

Injection time/s	Injection period/s	Dilution* (found)	RSD† (%)
25	35	6.8	2.0
10	15	8.8	1.0
10	20	12.6	0.9
5	20	24.2	1.2
2	20	59.1	1.2
1	20	114	1.8
1	25	224	2.1
1	30	272	1.9
1	20	610	2.3
1	30	910	3.0

\* Mean value of 20 replicate measurements.

† Relative standard deviation of 20 replicate measurements.

## Conclusions

Modifications of the merging stream and tandem injection steady-state concentration on-line dilution method were examined. Hydrodynamic injection using intermittent pumping with dual pumps can achieve tandem injection in an identical manner to conventional FI, and enable dilutions of up to about 1000 to be obtained with a double merging stream configuration. This method was examined with only constant-speed peristaltic pumps, but it should be possible to combine it with variable-speed flow channels.

The upper dilution range was extended for both the merging stream and the tandem injection configurations to cover all on-line dilutions that might be required practically. Variable-speed channels were either incorporated totally or only in part and permitted an increase in dilutions by a factor of about 2.5 over a constant-speed flow. However, when the variable-speed pump is used for all channels, all dilutions at the same over-all flow-rate can be achieved. The consequence of this approach is that the choice of an efficient mixing coil assembly can result in uniform precision, and a single flow module can produce any dilution over the whole range of dilutions. With partially variable flow channels, the over-all flow-rate becomes variable from one range of dilutions to another. Although a higher gain in the dilution factor is possible over a constant-speed flow, the repercussion is a considerable delay

**Table 5** Conventional tandem injection with a single-confluence junction followed by SFS-RM and constant-speed peristaltic pump operation. Time delay to reach steady-state concentration is 5–6 min.

Flow configuration*	Injection time/s	Injection period/s	Dilution† (found)	RSD‡ (%)
a	10	30	1120	1.6
a	5	30	2890	1.7
a	2	27	6240	1.4
a	2	27	6120	1.2
a	1	26	8990	1.8
a	1	26	8830	1.4
b	15	40	1680	1.5
b	15	40	1640	1.3
b	10	35	2380	1.5
b	10	35	2390	1.6
c	2	27	12480	1.5
c	2	27	12330	1.4
d	1	26	23200	1.1
d	1	27	23070	1.4

\* Flow-rates: a,  $U_{D_2}$  and  $U_{D_3}$ , 0.65; b,  $U_{D_2}$ , 1.21; and  $U_{D_3}$ , 2.42; c,  $U_{D_2}$  and  $U_{D_3}$ , 2.42; d,  $U_{D_2}$ , 2.42 and  $U_{D_3}$ , 3.71 ml min<sup>-1</sup>. Pump tubing diameters given in Fig. 4.

† Mean value of 20 replicate measurements.

‡ Relative standard deviation of 20 replicate measurements.

**Table 6** Conventional tandem injection with a single-confluence junction followed by SFS-RM using a partially variable speed operation of a number of flow channels (cf. Fig. 6) for an injection time of 1 s and an injection period of 26 s

Motor speed* (%)	Dilution† (found)	RSD‡ (%)
75	16100	2.3
75	16770	2.9
50	35230	2.2
50	38060	4.8
30	148700	1.4
28	168900	1.3
20	331900	1.0
20	305700	1.4

\* Time delay to reach steady-state concentration is approximately 7–8 min at 75%, 12–14 min at 50% and 25–30 min at 20% motor speed.

† Mean value of 20 replicate measurements.

‡ Relative standard deviation of 20 replicate measurements.

in the attainment of the steady-state concentration section, which may be partially overcome by several operating procedures.

The simplest and most powerful means of increasing on-line dilution is cascade dilution by stream flow splitting of the diluted sample solution, either by the merging stream approach or by tandem injection, followed by remerging with the diluent. A single SFS-RM operation can contribute as much as a dilution factor of 50 to the over-all dilution. Stream flow splitting and remerging is usually carried out smoothly, except for its combination with hydrodynamic tandem injection, where high back-pressure developed as a result of the large number of T-junctions required to carry out this combination.

In conclusion distinct units of flow systems that can contribute to steady-state concentration on-line dilution have been developed and were combined in a modular fashion to produce various dilutions. These combinations have the capability to cover, in practice, any required on-line dilution range.

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## References

- 1 Israel, Y., Lásztity, A., and Barnes, R. M., *Analyst*, 1989, **114**, 1259.
- 2 Israel, Y., and Barnes, R. M., *Analyst*, 1990, **115**, 1411.
- 3 van Staden, J. F., *Fresenius Z. Anal. Chem.*, 1985, **322**, 36.
- 4 Whitman, D. A., and Christian, G. D., *Talanta*, 1989, **36**, 205.
- 5 Basson, W. D., and van Staden, J. F., *Fresenius Z. Anal. Chem.*, 1980, **302**, 370.
- 6 Fernandez, A., Gomez-Nieto, M. A., Luque De Castro, M. D., and Valcarcel, M., *Anal. Chim. Acta*, 1984, **165**, 217.
- 7 Mindel, B. D., and Karlberg, B., *Lab. Pract.*, 1981, **30**, 719.
- 8 Clark, G. D., Růžicka, J., and Christian, G. D., *Anal. Chem.*, 1989, **61**, 1773.
- 9 Mindegaard, J., *Anal. Chim. Acta*, 1979, **104**, 185.
- 10 Garn, M. B., Gisin, M., Gross, H., King, P., Schmidt, W., and Thommen, C., *Anal. Chim. Acta*, 1988, **207**, 225.
- 11 Růžicka, J., and Hansen, E. H., *Anal. Chim. Acta*, 1980, **114**, 19.
- 12 Růžicka, J., and Hansen, E. H., *Anal. Chim. Acta*, 1983, **145**, 1.
- 13 Israel, Y., *Anal. Chim. Acta*, 1988, **206**, 313.

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