



University of  
Massachusetts  
Amherst

## On-line dilution for ICP-MS with a flow injection recirculating loop manifold

Item Type	article;article
Authors	Tyson, JF;Ge, HH;Denoyer, ER
Download date	2025-05-13 13:43:50
Link to Item	<a href="https://hdl.handle.net/20.500.14394/6306">https://hdl.handle.net/20.500.14394/6306</a>

# On-line Dilution for ICP-MS With a Flow Injection Recirculating Loop Manifold

JULIAN F. TYSON<sup>\*a</sup>, HONGHONG GE<sup>a</sup> AND ERIC R. DENOYER<sup>b</sup>

<sup>a</sup>Department of Chemistry, Box 34510, University of Massachusetts, Amherst, MA 01003-34510, USA

<sup>b</sup>The Perkin-Elmer Corporation, 761 Main Ave., Norwalk, CT 06859-0215, USA

A FI manifold consisting of a recirculating loop has been coupled to a plasma source mass spectrometer to provide successive on-line dilutions. Part of the loop is injected into the carrier stream followed by dilution, within the loop, of the remaining part with the carrier solution. For a manifold with a calculated dilution factor of 2.02 (based on the volume ratio), 10 successive injections gave a mean of 1.99 and a 95% confidence interval of  $\pm 0.065$  for the ratio of successive peak heights. The between-run precision for a particular peak height ranged from 1.7 to 3.2% relative standard deviation (RSD). In a study of the decay of the concentration oscillations in the recirculating loop, it was found that the reciprocal of the time to achieve uniform concentrations decreased linearly with increasing flow rate and decreasing loop volume. The dilution behaviors of 19 elements were studied. Of these, nine (Ag, Ba, Cr, Cu, Ni, Pb, Sb, Tl and U) could be diluted from 100 ppb by three orders of magnitude with a precision of 5% RSD or better, six (As, Cd, Co, Th, V, Zn) could be diluted over the same range with precisions between 5 and 10% RSD, and four elements (Be, Mo, Se and Hg) displayed a systematic decrease in the dilution factor which was interpreted as retention of these elements within the loop. The influence of a wine matrix on the determination of Ce was removed by five successive dilutions with a factor of 3.04 per injection for a total dilution factor of 260. For a total loop volume of 1–2 ml, rapid damping of the concentration oscillations could be produced by the destructive interference produced by a two-line network (split and confluence) with tube lengths of 50 and 25 cm.

**Keywords:** Inductively coupled plasma mass spectrometry; flow injection; dilution; recirculating loop; successive dilutions; calibration; wine

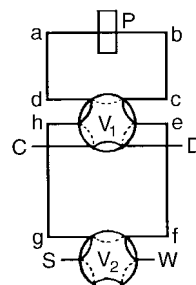
Dilution is used in analytical laboratories to prepare calibration standards, to bring sample concentrations within instrumental working ranges and/or to reduce matrix effects. There is, therefore, a need for automated on-line dilution techniques. Flow injection (FI) offers several ways to implement on-line dilution, including gradient dilution,<sup>1,2</sup> continuous dilution,<sup>3,4</sup> with manifolds incorporating mixing chambers,<sup>5</sup> variable tube dimensions,<sup>6</sup> merging zones,<sup>7,8</sup> networks<sup>9</sup> and variable injection volume dilution.<sup>10–13</sup> Most of these techniques are based on the dynamic dispersion characteristics of the FI process and thus are based on the requirements of precise timing of a particular operation (such as valve switching) and the requirement of precise pumping. For those systems based on the inherent dispersion coefficient of some particular manifold configuration, precise fluid delivery is still required as the dispersion coefficient is a function of flow rate. It is difficult to ensure good day-to-day reproducibility in flow delivery when peristaltic pumps are used. A recirculating loop FI manifold, which was first introduced for atomic spectrometry applications by Tyson *et al.*,<sup>14</sup> provides a new method for on-line dilution. The dilution factor is determined by the volumes of specified parts of the manifold. Such volumes are invariant parameters of a FI system.

In this work a recirculating loop manifold was coupled to a plasma source mass spectrometer and used (a) to provide data for calibration curves with a single standard and (b) to reduce matrix effects with successive dilutions, a requirement of EPA ICP-MS methods 200.8 and 6020M. Matrix effects generally depend on the total matrix concentration rather than relative concentration of analyte and matrix, and therefore, in general, matrix effects may be removed by successive dilution. The performance of several mixing devices for increasing the speed of the dilution process was evaluated. These devices included a simple split and confluence network to provide concentration damping by destructive interference.

## EXPERIMENTAL

### Principle of the Recirculating Loop Dilution Manifold

A schematic diagram of a recirculating loop manifold constructed with two six-port rotary valves is shown in Fig. 1. The sample is loaded into the loop when both valves are in the 'load' position (solid line) and the pump, P, is on. When valve 2 is switched to the closed position (dashed line), a closed loop is formed in which the sample solution circulates. When valve 1 is switched to the inject position (dashed line), the sample in the 'bottom' portion of the loop (efgh) will be injected into the carrier stream, pumped from C to D and transported to the detector. This operation fills the 'bottom' portion of the loop with carrier. When valve 1 is switched back to the 'load' position, the sample in the 'upper' portion of the loop (abcd) mixes with the carrier in the 'lower' portion of the loop until a homogeneous diluted solution is obtained. Valve 1 is then again switched into the inject position which introduces the diluted sample to the detector. Successive dilution can thus be performed by repeatedly actuating valve 1. The dilution factor ( $d$ ) of the manifold for one actuation of the valve is the ratio of the volume of the total loop (abcefg) to that of the volume of the 'upper' portion of the loop. The dilution factor for  $n$  successive actuations is  $d^n$ . Thus dilutions by large factors can be obtained by repetitive actuation of valve 1. For example, if  $d = 3$ , dilution by a factor of over 2000 is obtained after six injections.



**Fig. 1** Schematic diagram of a recirculating loop manifold: S, sample; C, carrier; P, peristaltic pump; D, detector;  $V_1$  and  $V_2$  six-port rotary valves.

## Spectrometers

The plasma source mass spectrometer used was a Perkin-Elmer (Norwalk, CT, USA) SCIEX model ELAN-5000. The parameter settings used are shown in Table 1. A Hewlett-Packard (Avondale, PA, USA) model HP8452A diode array spectrophotometer was used to study the processes of mixing in the loop.

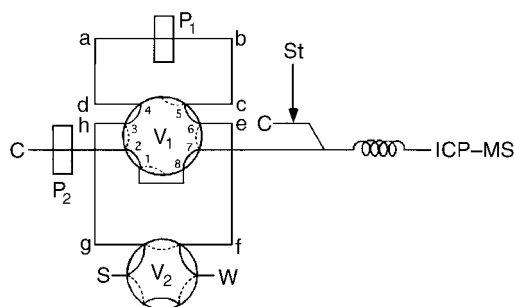
## FI Manifolds

The recirculating loop manifold for ICP-MS, shown in Fig. 2, was constructed from a manually operated two-way, six-port valve (Rheodyne, Cotati, CA, USA) and a Perkin-Elmer FIAS-200 FI analyzer fitted with two four-channel peristaltic pumps and a two-layer, eight-port rotary valve. The upper loop consisted of 35 cm of Tygon tubing of id 1.14 mm, together with 25 cm of PTFE tubing of id 0.76 mm. The lower loop consisted of 110 cm of 0.76 mm id PTFE tubing. The FIAS-200 instrument was remotely controlled by the ELAN-5000 software. Internal standards or spike standards were introduced to the flow system by a six-port rotary injection valve (P.S. Analytical, Orpington, Kent, UK) which was remotely controlled by the FIAS-200 unit *via* a built-in electronic switch closure. The volume of the internal or spike standard injected was 156  $\mu$ l.

The FIAS-200 programs are shown in Tables 2 and 3. Table 2 contains the program for measurement of an undiluted sample (the first injection) and Table 3 contains the program

**Table 1** ELAN-5000 operating conditions and data acquisition parameters

Forward rf power	1000 W
Plasma Ar flow	15 l min <sup>-1</sup>
Auxiliary Ar flow	0.8 l min <sup>-1</sup>
Carrier (nebulizer) Ar flow	0.75–0.95 l min <sup>-1</sup>
Sample and skimmer cones	Ni
Data acquisition	transient multichannel analysis
Scan mode	peak hop transient
Measurement	one MCA channel (spectral peak average)
Dwell time	40 ms



**Fig. 2** The recirculating loop manifold built incorporating the FIAS-200 unit: P<sub>1</sub> and P<sub>2</sub> are peristaltic pumps on the FIAS-200 unit; V<sub>1</sub> is an eight-port, two-layer rotary valve on the FIAS-200 unit; V<sub>2</sub> is a manually operated two-way, six-port valve; C, carrier; S, sample; W, waste; ICP-MS, detector; St: standard solution (spike or internal standard).

**Table 2** FIAS program for the first peak in the successive dilutions

Step	ICP-MS reading	Time/s	P <sub>1</sub> (rpm)	P <sub>2</sub> (rpm)	V <sub>1</sub>	V <sub>2</sub>	Electronic valve
1	no	30	60	120	recirculate	open	load
2	no	5	0	0	recirculate	closed	load
3	yes	5	120	0	inject	closed	load
4	yes	25	120	0	inject	closed	inject

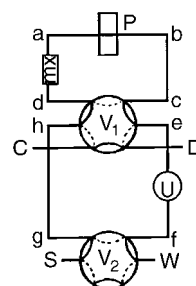
**Table 3** FIAS program for successive dilutions

Step	ICP-MS reading	Time/s	P <sub>1</sub> (rpm)	P <sub>2</sub> (rpm)	V <sub>1</sub>	V <sub>2</sub>	Electronic valve
1	no	20–60	60	120	recirculate	closed	load
2	no	20–60	60	120	recirculate	closed	load
3	yes	5	120	0	inject	closed	load
4	yes	25	120	0	inject	closed	inject

for a successively diluted sample. In step 1 of Table 2, valve 1 was in the recirculate position and valve 2 was open (solid lines). Pump 1 was for the carrier introduction and pump 2 was for the sample loading. In step 2, pump 2 was stopped for 5 s and the six-port valve (V<sub>2</sub>) was turned to the closed position (dashed line). A closed loop, filled with concentrated sample or standard, was formed at this stage. Valve 2 was retained in the closed position (dashed line) for the rest of the experiment. In step 3, the eight-port valve (V<sub>1</sub>) was turned counter clockwise to the inject position (dashed line), allowing the sample in the bottom portion of the loop (23hgfe67) to be flushed out by the carrier. The signal collection process was started at the beginning of this step. The holes of the eight-port valve are not equally spaced, the distance between ports 4 and 5, and 1 and 8, being larger than the distances between the other ports. So in the inject position, ports 4 and 8 did not line up. After 5 s, the six-port injection valve (shown as St in Fig. 2) was turned to the inject position (step 4), then the internal standard or spike standard was merged with the sample at the confluence point, mixed in a 100 cm long coiled Teflon open-tubular reactor (id 0.76 mm) and finally flushed into the plasma for 25 s.

The program for the successive dilutions is shown in Table 3. In steps 1 and 2, V<sub>1</sub> was in the recirculate position (solid line). Pump 1 was set at 60 rpm (2 ml min<sup>-1</sup>) and pump 2 was at 120 rpm (4 ml min<sup>-1</sup>). The sample remaining in the 'upper' portion of the loop (abcd) was mixed with the carrier in the 'bottom' portion of the loop (efgh). The recirculating time for both steps could be varied according to the speed of the mixing process, which depended on the flow rate, loop volume, mixers used and expected precision. For example, for a manifold with 1.45 ml total loop volume and 3.38 dilution factor, a precision of 4.5% RSD was achieved with a 40 s recirculating time at a recirculating flow rate of 4 ml min<sup>-1</sup>.

The manifold for the study of the mixing processes within the recirculating loop is shown in Fig. 3. The valves were both manually operated six-port rotary valves (Rheodyne model 5020). The flow cell (Pye Unicam, Cambridge, UK) of pathlength 1.0 cm and volume 18  $\mu$ l, was mounted in the HP8452A diode array spectrophotometer. The performance of a variety of mixing devices, including wide-bore tubing, mixing chambers,<sup>15</sup> split and confluence networks, was studied. Both the flow cell and the mixing devices were located in the recirculating loop.



**Fig. 3** The recirculating loop manifold for the study of the mixing process: S, sample; C, carrier; P, peristaltic pump; W, waste; V<sub>1</sub> and V<sub>2</sub>, six-port rotary valves; U, flow cell in visible spectrometer; mx, mixing devices.

## Reagents

Standard solutions of metals for the ICP-MS experiments were prepared from 1000 ppm plasma grade standards obtained from Johnson Matthey (Wayne, PA, USA). Nitric acid, 1%, (purified by a quartz sub-boiling system) in distilled deionized water was used as diluent and carrier. Vendange wine with an alcohol content of 13.2% was used as the sample and was purchased from a local liquor store. Tartrazine (Eastman Kodak, Rochester, NY, USA) was used in the visible absorption experiments as a tracer to follow the mixing processes in the recirculating loop.

## Development of the System

The analytical performance of the recirculating loop was examined for successive dilutions of a 91.5 ppb cerium standard solution. Ten successive dilutions were carried out which diluted the 91.5 ppb Ce standard solution to 0.089 ppb. The accuracy of the dilution procedure was evaluated by comparing the observed dilution factor with the calculated dilution factor. The observed dilution factor was the ratio of the ICP-MS signals for two successive dilutions and the calculated dilution factor was the ratio of the volume of the total loop to that of the upper portion of the loop. The loop volume was determined by a photometric procedure using tartrazine as the solute. The entire loop was filled with a 49.5 ppm tartrazine solution. The solution in the bottom loop (or the whole loop) was then washed out with distilled water into a 25 ml calibrated flask, and diluted to the mark. The absorbance of the diluted solution was measured and the concentration determined from a calibration curve. The 'upper' loop volume was calculated as the difference between the whole loop volume and the 'bottom' loop volume.

The reproducibility of the process was evaluated by running three series of successive dilutions. The calculated dilution factor and the total loop volume of the manifold used were 3.04 and 1.27 ml, respectively. The recirculating time for the mixing process was set at 120 s.

The dilution behavior of elements which can be determined by EPA 200.8 (a method to determine trace elements in water and waste by ICP-MS) was examined. The concentration range covered for each element was from about 100 ppb to the total recoverable detection limit (TRDL, the detection limit for a procedure to recover the analyte in all chemical forms) specified in the method protocol. For example, the TRDL of Ag is specified as 0.1 ppb. The TRDL values specified cover the range from 0.1 to 7.9 ppb. The loop parameters were the same as above.

External calibration curves for Ce and Ba were constructed simultaneously from a single standard containing 91.5 ppb of each element. The dilution factor of the manifold was 2.40 and the total loop volume was 0.84 ml. The recirculating time for the mixing process was set at 120 s.

An internal calibration curve for Ce was also constructed with a single standard. The internal standard Tb was introduced to the flow system by the six-port valve which was remotely controlled by the FIAS-200 so that the manifold operated in a merging zones mode. The concentrations of Ce and Tb were 43.4 and 43.7 ppb, respectively. The dilution factor of the recirculating loop was 3.04 and the total loop volume was 1.27 ml. The recirculating time was set at 120 s. The injection of the Tb internal standard was delayed by 5 s following the actuation of the eight-port valve.

## Recovery of Cerium From a Wine Sample With Successive Dilutions

The reduction of matrix effects by successive dilution was also studied by examining the recovery of a cerium standard from

a wine sample. The manifold used was the same as in the internal calibration construction. The original wine sample was loaded into the loop and the portion in the bottom loop was injected into the carrier and merged with 156  $\mu$ l of a 43.7 ppb Ce standard solution. The signal intensities for each successive diluted peak were recorded as  $I_1$  to  $I_n$ . When 1% nitric acid was used as the spike standard, a series of diluted peak intensities were recorded (as  $B_1$  to  $B_n$ ) corresponding to signals for successively diluted wine samples. When 1% nitric acid was used as the sample and Ce as the spike standard, peak intensity was recorded as  $I_0$ , corresponding to the signal for 156  $\mu$ l of a 43.7 ppb Ce standard without any matrix effect. The recovery of Ce from each successive diluted wine sample was calculated as  $(I_i - B_i)/I_0 \times 100\%$ .

## Improvement of the Mixing Efficiency

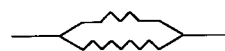
The mixing between sample and diluent in the recirculating loop was studied by visible absorption spectrometry. A solution of 10 ppm tartrazine was used as the sample and distilled water as the diluent. The spectrometer was set at 426 nm where tartrazine has a strong absorption peak. The kinetics program was used, which displayed absorbance as a function of time. The lower loop consisted of 135 cm of 0.76 mm id PTFE tubing. The upper loop consisted of 13.5 cm of Tygon tubing of id 2.06 mm, 10 cm of 0.76 mm id tubing and an 18  $\mu$ l flow cell. Parameters which affect the mixing process were investigated. These included recirculating flow rate, loop volume and, inserted into the upper loop, several mixing devices to speed up the mixing of the sample and the diluent. These mixing devices included a well stirred chamber (1 ml volume), a short fat tube (1.2, 2.8 or 5.6 cm long and 4.55 mm id) and a split-confluence device, shown in Fig. 4, consisting of two open tubular reactors (0.76 mm id) of different lengths connected by two 120° three-way Omnifit connectors. Several experiments were performed with the same relative lengths (2:1) of tubing, for which the length of the shorter arm was 12.5, 25, 50, 75 or 100 cm.

## RESULTS AND DISCUSSION

### Accuracy and Reproducibility

The peak intensities, observed dilution factors and calculated concentrations for 10 successive dilutions of the 91.5 ppb Ce solution are given in Table 4. The average observed dilution factor was 1.99, with 4.6% RSD. The calculated dilution factor was 2.02 (the ratio of the total loop volume of 0.97 ml to that of the upper loop volume of 0.48 ml). Good agreement was achieved between the calculated and the observed dilution factor with no difference at the 95% confidence level.

The reproducibility of the dilution process for three repeated series of successive dilutions is shown in Table 5. The reproducibility of dilution factors between different series was as good as that of the successive dilution factors in the same series. The apparently lower between-run RSD is probably not significant.



**Fig. 4** A split-confluence device. The back-pressures of the two branches are different because of the differences in lengths and so the flow rate is slower in the longer branch. Regardless of the flow rates, the concentrations in the two lines are the same, but the oscillations become progressively out of phase during passage through the device. The lengths are chosen so that destructive interference occurs at the confluence point.

**Table 4** Results for ten successive dilutions of a Ce standard

Peak No.	Intensity/counts s <sup>-1</sup>	d <sub>i</sub> *	Concentration (ppb)
1	3.47 × 10 <sup>5</sup>		91.5
2	1.70 × 10 <sup>5</sup>	2.04	45.8
3	8.62 × 10 <sup>4</sup>	1.97	22.9
4	4.44 × 10 <sup>4</sup>	1.94	11.4
5	2.18 × 10 <sup>4</sup>	2.04	5.72
6	1.17 × 10 <sup>4</sup>	1.86	2.86
7	5.42 × 10 <sup>3</sup>	2.16	1.43
8	2.75 × 10 <sup>3</sup>	1.97	0.715
9	1.47 × 10 <sup>3</sup>	1.87	0.358
10	759	1.94	0.179
11	368	2.06	0.089

\* Dilution factor based on ratio of successive peaks.

**Table 5** Reproducibility of successive Ce dilutions

Run number	Peak ratio dilution factor					RSD (%)
	d <sub>1,2</sub> *	d <sub>2,3</sub>	d <sub>3,4</sub>	d <sub>4,5</sub>	d <sub>average</sub>	
I	2.82	2.92	3.05	2.93	2.93	3.2
II	2.80	3.00	2.92	3.03	2.94	3.5
III	2.91	3.11	2.99	2.96	2.90	2.8
d <sub>I-III average</sub>	2.84	3.01	2.99	2.97	—	—
RSD <sub>I-III</sub> (%)	2.1	3.2	2.2	1.7	—	—

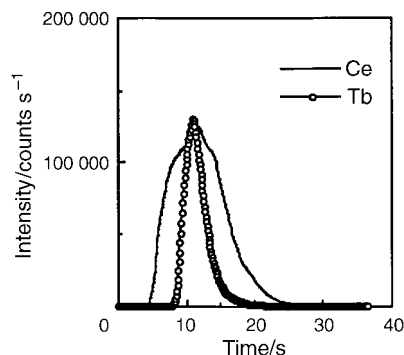
\* Dilution factors based on the ratio of successive peaks as indicated by the appropriate subscripts.

### Dilution Behavior of Various Elements

Of the 19 elements examined, most exhibited linear dilution behavior with good precision from about 100 ppb to the EPA 200.8 TRDL. The RSDs of observed dilution factors were less than 5% for the elements <sup>107</sup>Ag, <sup>52</sup>Cr, <sup>63</sup>Cu, <sup>60</sup>Ni, <sup>121</sup>Sb, <sup>(206+207+208)</sup>Pb, <sup>137</sup>Ba, <sup>238</sup>U and <sup>205</sup>Tl. Less than 10% RSD was achieved for the elements <sup>59</sup>Co, Cd[<sup>111</sup>C-0.073(<sup>108</sup>C-0.712 × 10<sup>6</sup>C)], <sup>232</sup>Th, <sup>66</sup>Zn, <sup>75</sup>As and V[<sup>51</sup>C-3.127(<sup>53</sup>C-0.113<sup>52</sup>C)], where C represents the counts s<sup>-1</sup> at the specified mass to charge ratio, if diluted from about 100 ppb to the TRDL. Less than 5% RSD was obtained for these elements when diluted to about 5 ppb. The dilution factors of selenium, beryllium, molybdenum and mercury (not covered by the EPA 200.8 method) kept decreasing with successive dilutions. This may have been due to adsorption of these elements within the loop, as long-tailed FI profiles were observed.

### External and Internal Calibration Curves From a Single Standard

External calibration curves for <sup>140</sup>Ce and <sup>137</sup>Ba were constructed simultaneously. Linear calibration curves were obtained. An unweighted least squares fitting procedure gave equations for the two lines as follows: <sup>140</sup>Ce,  $y = 162 + 7660x$  and for <sup>137</sup>Ba,  $y = -84 + 888x$  where  $x$  is the calculated concentration in ppb, assuming the dilution factor was 2.40 (the calculated dilution factor of the manifold), and  $y$  is the observed intensity for each dilution in units of counts s<sup>-1</sup>. The correlation coefficient of each line was 1.000. A linear internal calibration curve was also constructed for Ce with Tb as the internal standard. The overlap of the two FIA peaks is shown in Fig. 5, from which it can be seen that the Tb and Ce solutions were well mixed and reached the plasma at the same time. The equation of this line was (unweighted least squares fit),  $y = -0.0003 + 0.0252x$ , where  $x$  is the calculated concentration of Ce in ppb and  $y$  is the intensity ratio of <sup>140</sup>Ce to <sup>159</sup>Tb. The correlation coefficient was 0.9997. The 95% confi-



**Fig. 5** The overlap of Ce and Tb FIA peaks produced by the merging zones manifold for internal calibration.

dence intervals about the intercepts for all three lines included the origins.

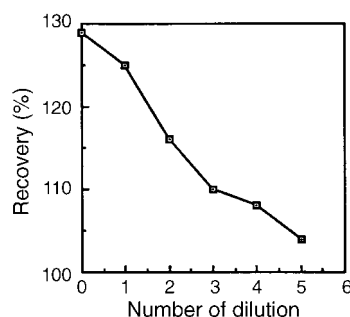
### Recovery of Cerium From a Wine Sample With Successive Dilutions

In EPA ICP-MS methods, dilution is often needed to reduce matrix effects. For example, as stated in EPA 200.8, section 10.6: 'If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect'. The specified limits are 75–125%. The reduction of matrix effects by successive dilution was demonstrated by a study of the recovery of Ce from a wine sample. The results are shown in Fig. 6. It was found that wine had an enhancement effect in the determination of Ce. The recovery of Ce from the concentrated wine was 129%, which decreased to 110% with three successive dilutions, and finally to 104% with two more successive dilutions. The final value is well within the limits specified in EPA method 200.8.

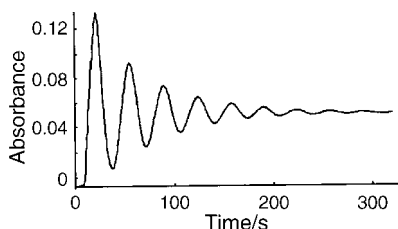
### Improvements in the Mixing Efficiency

A typical concentration oscillation, tracked by the absorbance of the tartrazine solution, is shown in Fig. 7. It was found that the concentration oscillation decay time,  $t$  (time in s taken for the oscillation amplitude to decrease to 1% of the final absorbance signal), decreased linearly with (a) increasing recirculating flow rate,  $Q$ , (over the range 1.00–4.00 ml min<sup>-1</sup>) and (b) decreasing loop volume,  $V_i$ , (over the range 1.30–2.30 ml). The equations of the two lines were as follows (unweighted least squares fit),  $1/t = 4.48 \times 10^{-4} + 8.0 \times 10^{-4} Q$  (for which the correlation coefficient was 0.999) and  $1/t = 7.8 \times 10^{-3} - 2.63 \times 10^{-3} V_i$  (for which the correlation coefficient was also 0.999).

The oscillation decay times for solutions of different concentration were found to be the same for absorbances between 0.1 and 0.9. When the absorbance was too low, the oscillation



**Fig. 6** The recovery of Ce from a wine sample as a function of successive dilutions.



**Fig. 7** Tartrazine concentration oscillations in a recirculating loop. The upper loop consisted of 35 cm of Tygon tubing with 25 cm of 0.76 mm id PTFE tubing. The lower loop consisted of 220 cm of 0.76 mm id PTFE tubing and an 18  $\mu$ l flow cell.

decayed rapidly into the noise. All three mixing devices speeded up the mixing process, but it was found that the mixing chamber caused problems with air bubbles. The split-confluence mixer was more efficient than the closed loop alone or the loop containing the short, fat tube. The oscillation decay times were 90, 62 and 52 s for the simple loop, the loop plus 1.2 cm of short, fat tube (the most efficient of the three reactors evaluated) and the split-confluence device with lengths 25 and 50 cm, respectively. Because of the different coil lengths in the split and confluence devices, the solutions in the two branches had different concentration oscillation profiles at the merging point. The addition of the two out-of-phase concentration oscillation profiles resulted in a damped oscillation profile. Both the absolute and relative lengths of the two branches will affect the mixing process. A ratio of 1:2 was found the best for the relative length. The optimal absolute length of the branches will vary with the total loop volume. Lengths of 50 and 25 cm coils (id 0.76 mm) were found to be suitable for a loop of total volume of 1–2 ml. This split-confluence mixer was used in the manifold coupled to the plasma source mass spectrometer. For a mixing time of 40 s, an RSD of 4.5% was obtained with three successive dilutions of 43.7 ppb Ce to 1.1 ppb, and for a mixing time of 60 s an RSD of 2.8% with four dilutions to 0.33 ppb was obtained. The total loop volume of the manifold was 1.45 ml.

A theoretical treatment of the mixing in a recirculating loop should be possible, but is considered beyond the scope of this publication. A suitable basis for such a treatment might be calculations of the residence times for which the volume occupied by the sample bolus became multiples of the loop volume. A useful starting point for these calculations would be the description of laminar flow in closed circular conduits provided by Vanderslice *et al.*<sup>16</sup>

## CONCLUSIONS

A recirculating loop manifold can provide accurate and precise on-line dilution suitable for use with ICP-MS. The manifold can be used to obtain calibration data from a single concentrated standard, and to reduce matrix effects by successive dilutions.

The provision and maintenance of the ELAN-5000 and FIAS-200 instruments by Perkin-Elmer is gratefully acknowledged.

## REFERENCES

- Olsen, S., Ruzicka, J., and Hansen, E. H., *Anal. Chim. Acta*, 1982, **136**, 101.
- Yang, J., Ma, C., Zhang, S., and Shen, Z., *Anal. Chim. Acta*, 1990, **235**, 323.
- Tyson, J. F., and Appleton, J. M. H., *Talanta*, 1984, **31**, 9.
- Tyson, J. F., Appleton, J. M. H., and Idris, A. B., *Anal. Chim. Acta*, 1983, **145**, 159.
- Beinrohr, E., Csemi, P., and Tyson, J. F., *J. Anal. At. Spectrom.*, 1991, **6**, 307.
- Tyson, J. F., Mariara, J. R., and Appleton, J. M. H., *J. Anal. At. Spectrom.*, 1986, **1**, 273.
- Zagatto, E. A. G., Krug, F. J., Bergamin, H. F., Jorgensen, S. S., and Reis, B. F., *Anal. Chim. Acta*, 1979, **104**, 279.
- Mindegaard, J., *Anal. Chim. Acta*, 1979, **104**, 185.
- Tyson, J. F., and Bysouth, S. R., *J. Anal. At. Spectrom.*, 1988, **3**, 211.
- Bergamin, H. F., and Pessenda, L. C. R., *Anal. Chim. Acta*, 1981, **123**, 221.
- Sherwood, R. A., Rocks, B. F., and Riley, C., *Analyst*, 1985, **110**, 493.
- de la Guardia, M., Morales-Rubio, A., Carbonell, V., Salvador, A., Burguera, J. L., and Burguera, M., *Fresenius' J. Anal. Chem.*, 1993, **345**, 579.
- Fang, Z., Welz, B., and Sperling, M., *Anal. Chem.*, 1993, **65**, 1682.
- Tyson, J. F., Bysouth, S. R., Grzeszczyk, E. A., and Debrah, E., *Anal. Chim. Acta*, 1992, **261**, 75.
- Tyson, J. F., *Analyst*, 1987, **112**, 523.
- Vanderslice, J. T., Rosenfeld, A. G., and Beecher, G. R., *Anal. Chim. Acta*, 1986, **179**, 119.

Paper 6/08601B

Received December 24, 1996

Accepted May 27, 1997