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Technical Note

Benefits of a Segmented Washout Stream with Discrete Sample Introduction Systems for ICP-MS

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INTRODUCTION

High matrix samples, such as seawater and biological materials, pose washout problems with most sample introduction systems for inductively coupled plasma-mass spectrometry (ICP-MS), which can lead to carryover between samples for a given method. Additionally, poor washout of high matrices can lead to poor method stability over relatively long runs.

A segmented stream of rinse solution minimizes diffusion back through the uptake path by providing physical barriers to diffusion. In the form of air-liquid interfaces, this enhances washout characteristics of sample introduction systems.

Similarly, decreasing the inner diameter of uptake tubing, especially sample loops in discrete sampling systems such as the Teledyne CETAC *ASXpress Plus*, increases the linear velocity of the liquid stream for a given volumetric flow-rate. This also aids in overcoming diffusion rates and enhancing washout characteristics.

METHODOLOGY

Testing was performed using a Thermo Scientific X-Series II quadrupole ICP mass spectrometer (Thermo Scientific, Hemel Hempstead, UK) coupled to a Teledyne CETAC ASX-520 autosampler. Samples were introduced to the ICP using a borosilicate glass nebulizer, *via* an EzyFit* coupling, and a cooled spray chamber. The *ASXPRESS PLUS* was placed between the autosampler and the nebulizer when in use.

A 10 ppb tuning solution was used to assess sample uptake and washout characteristics through both the standard and *ASXPRESS PLUS* sample introduction setups. Additional parameters are listed in Table 1 below.

Table 1 – Test Parameters for the X-Series II and the *ASXPRESS PLUS*

Thermo Scientific X-Series II			Teledyne CETAC ASXpress Plus	
Cool Gas Flow	13.00	L min^{-1}	Wash Station Purge Delay	1.0 s
Auxiliary Gas Flow	0.70	L min^{-1}	Loop Load (1.02 ml loop)	3.0 s
Nebulizer Gas Flow	0.83	L min^{-1}	Stir Delay	0.0 s
RF Power	1400	W	Probe Wash	3.0 s
Dwell Time	50	ms	Rinse Station Fill	10.0 s
Carrier Flow Rate	~ 300	µl min^{-1}	Pump Timeout	90.0 s

Sample was introduced into the system and the real-time display was monitored for changes in signal. Four time points of interest were noted:

1. Sample Uptake Delay: the time taken for the signal to rise above background to indicate the sample ions had reached the detector.
2. Stabilization Delay: the time taken for the mass flux into the plasma to stabilise and produce a steady signal at the detector.
3. Sampling Time: the time for which a steady signal was being obtained by the ICP-MS.
4. Washout Delay: the time taken for the signal at the detector to fall back to baseline levels from the end of the sampling time.

RESULTS AND DISCUSSIONS

The normal uptake profile of the X-Series II is shown in Figure 1 below. The acquisition delay is approximately 105 s, which comprised 95 s sample uptake delay and 10 s stabilization. The sample probe was moved to rinse after 70 s, resulting in a sampling time of 60 s. Washout of the system also took 105 s, starting from 165 s and reaching baseline at 270 s.

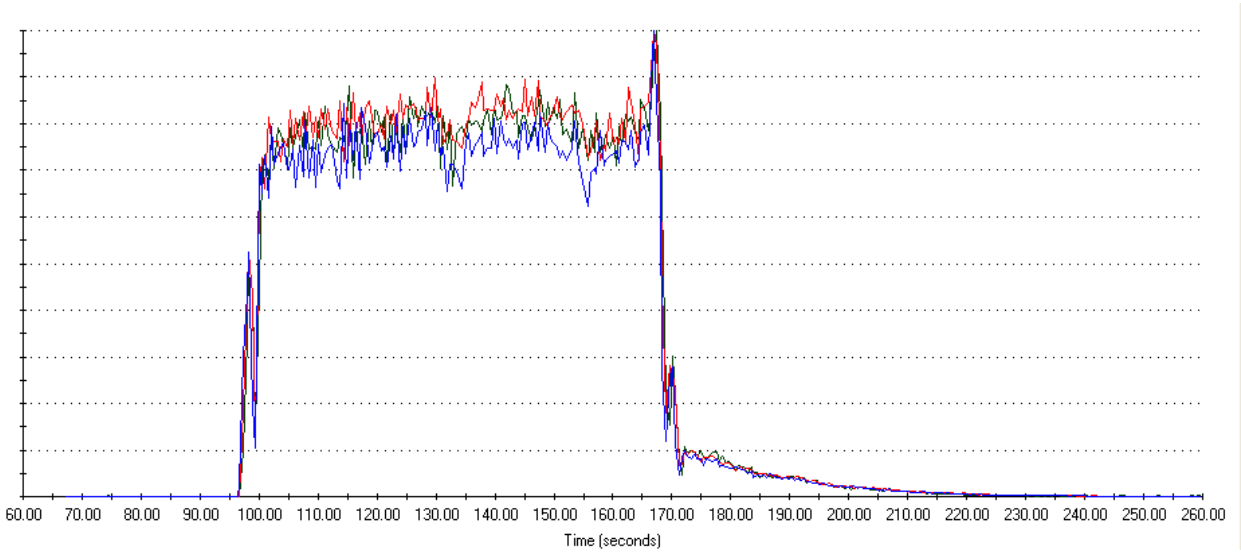

Figure 1 – Normal uptake profile of a 10 ppb tuning solution using the standard introduction system using a contiguous carrier stream pumped at ~300 µl min^{-1}

The standard introduction system introduces an air-liquid interface at the front and back end of the sample slug. This minimizes diffusion downstream relative to sample flow and results in a sharp rise in signal (after an air-spike seen at approx. 95 s). Stabilization is also sharp due to minimal forward diffusion. At the back end of the slug, contact between the sample and the carrier solution is limited to a thin film of sample deposited on the inner surfaces of the sample uptake path. This is picked up by the contiguous carrier stream and subsequently diffuses back upstream with respect to carrier flow, resulting in a relatively long washout phase.

With the *ASXPRESS PLUS* system in place, configured with the aqueous sample valve and the aqueous sample loop, the sample uptake delay was reduced to 11 s; however, the design of the *ASXPRESS PLUS* switching valve means there are no air-liquid interfaces between the carrier flow and the sample slug. Additionally, the inner diameter of the loop is much larger than that of the standard uptake probe (~2.5 mm and ~1.0 mm respectively). Both these factors increase the degree of diffusion downstream (relative to sample flow) and consequently the stabilization time increased to approximately 35 s (see Figure 2 below).

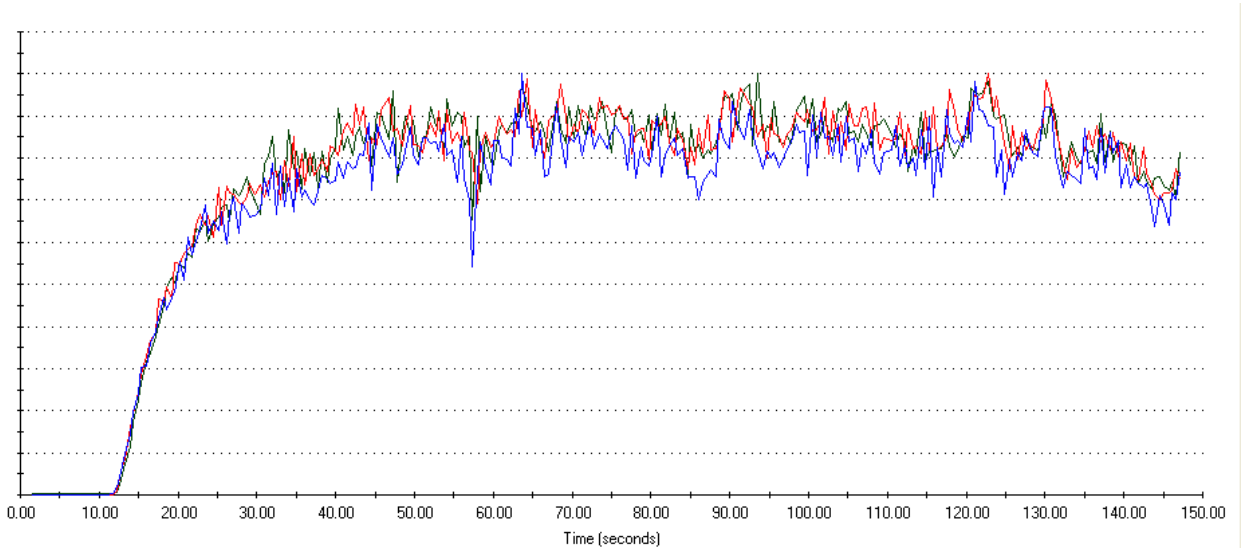

Figure 2 – Uptake profile of 10 ppb Tuning Solution using the *ASXPRESS PLUS* system configured with an aqueous switching valve and a 1.02 ml aqueous sample loop using a contiguous carrier stream pumped at ~300 µl min-1

The sampling time of this system appeared to be 85 s; however, at the chosen flow-rate and loop volume, this should have been approximately 200 s. Due to the upstream diffusion of the sample, the sample signal started its apparent washout phase much earlier than anticipated, which means choosing a loop volume using the method sampling time and the carrier stream flow-rate would yield poor precision.

The washout time of this system was in excess of 180 s, as illustrated in Figure 3 below. This performance is much worse than the standard sample introduction system, with baseline being achieved around 470 s after the signal is seen to drop off. Back-diffusion of the sample upstream in the relatively wide-bore sample loop lengthens the washout phase considerably.

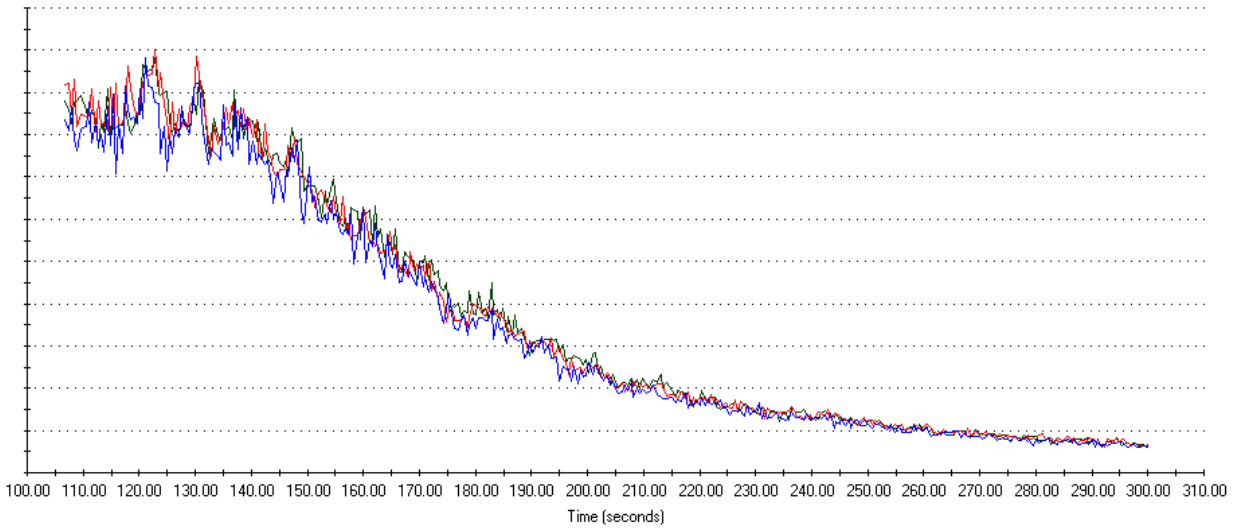

Figure 3 – Washout profile of 10 ppb tuning solution using the *ASXPRESS PLUS* system configured with an aqueous switching valve and a 1.02 ml aqueous sample loop using a contiguous carrier stream pumped at ~300 µl min^{-1}

Minimizing the inner diameter of the sample loop (using an 'oils' sample loop at approx. 1 mm) yielded a similar uptake profile. The sample uptake delay was 11 s with a slightly reduced stabilization delay of approximately 30 s and a slightly increased sampling time of 95 s. The washout profile, however, was improved significantly with a washout time of 230 s, with baseline achieved 360 s after the tuning solution was initially sampled. This time is still greater than the standard system's washout time, however, and the sampling time is still much lower than expected.

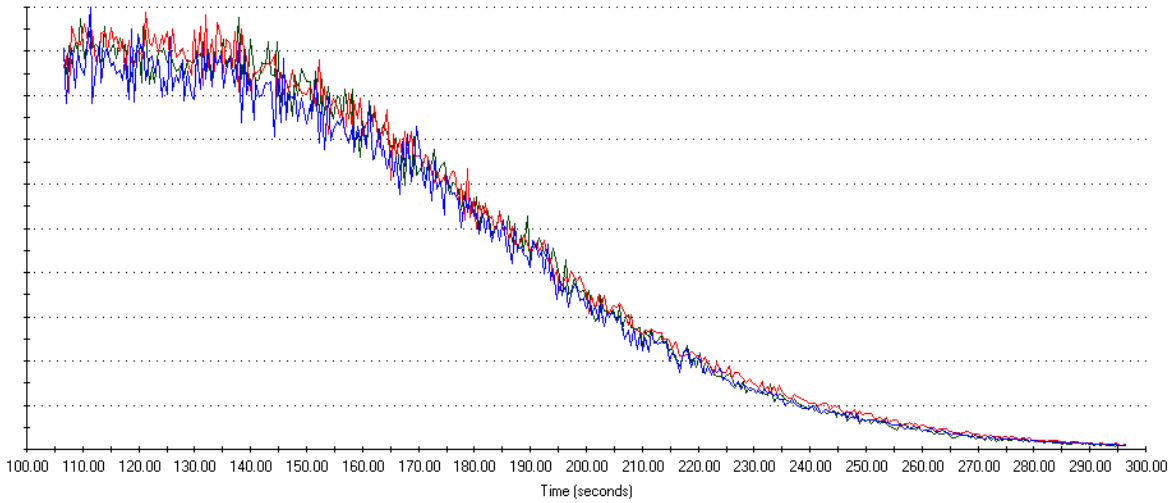

Figure 4 – Washout profile of 10 ppb tuning solution using the *ASXPRESS PLUS* system configured with an aqueous switching valve and a 1.02 ml oils sample loop using a contiguous carrier stream pumped at ~300 µl min^{-1}

Numerical simulations of the two sample loops show that, for a given sample type and flow rate, the thinner oils loop would be washed out more quickly than the aqueous loop due to diffusion processes having a more significant effect in the larger diameter tubing (see Figure 5 below). The calculated washout profiles from the exit planes of the loops are in good agreement with the experimental data gathered above, showing a sharper washout phase for the thinner I.D. loop and a return to baseline at an earlier time.

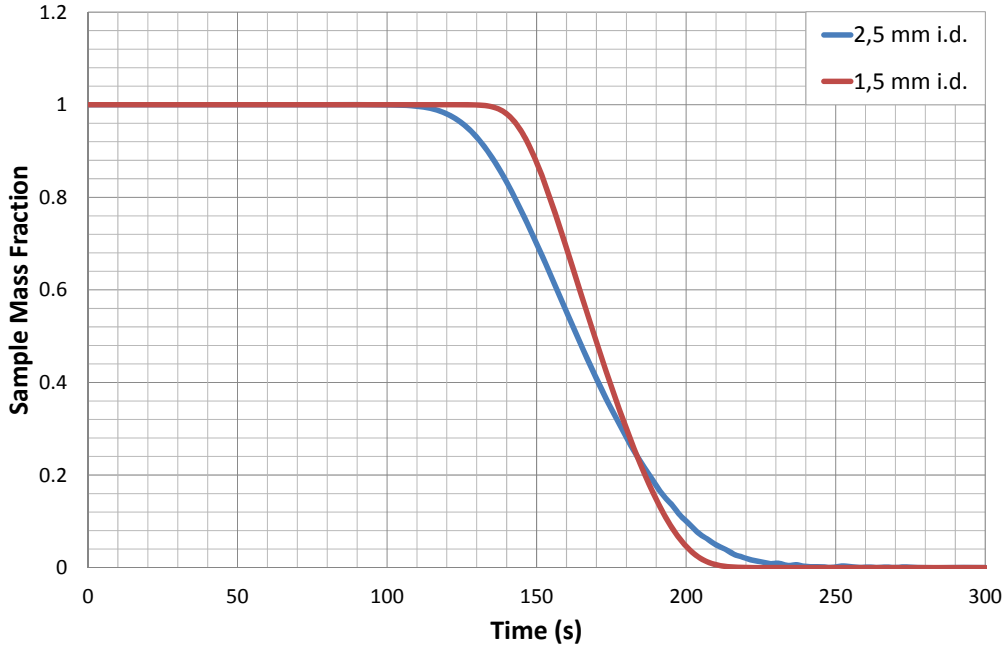

Figure 5 – A graph to show how sample mass fraction varies with time at the exit plane of two 1 ml sample loops of varying inner diameter, using ethanol as a sample and water as a contiguous carrier solution pumped at 300 µl min^{-1}

Using a segmented carrier stream introduces a series of air-liquid barriers in the front and back end of the sample slug in the uptake path. These barriers minimize diffusion by limiting contact between sample and carrier solution. This results in a much sharper uptake profile. Using the aqueous loop on the aqueous valve, the sample uptake delay is increased to approximately 20 s, but the stabilization delay is now reduced to 7 s (see Figure 6 below).

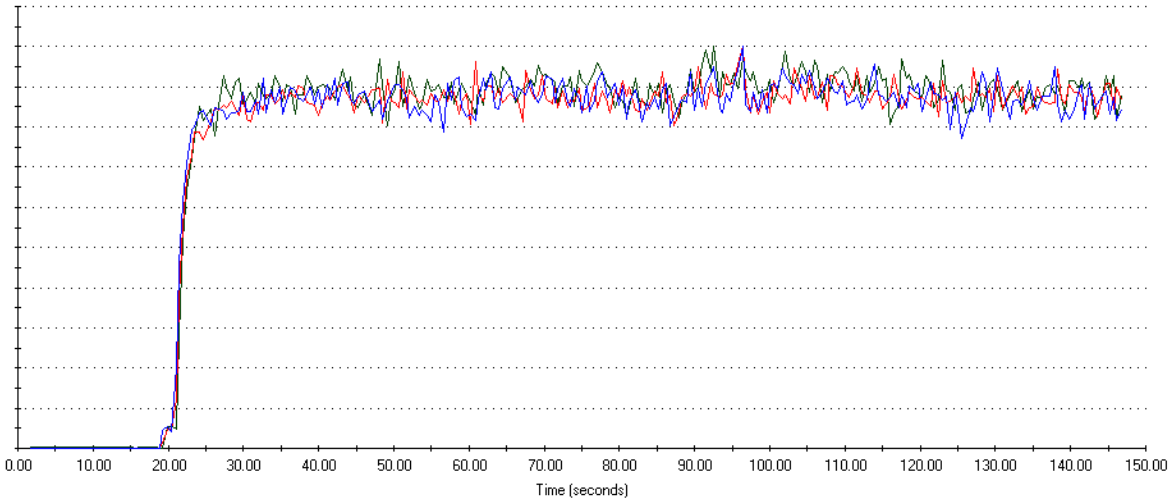

Figure 6 – Uptake profile of 10 ppb tuning solution using the *ASXPRESS PLUS* system configured with an aqueous switching valve and a 1.02 ml aqueous sample loop using a segmented carrier stream pumped at ~300 µl min^{-1}

The sampling time is now increased to 183 s, which is much closer to the time predicted using the sample loop volume and the carrier stream flow-rate. Contact only occurs with a thin film of sample, deposited on the inner surface of the sample uptake tubing, and the carrier solution, which now a small slug. Any diffusion is now limited in space by the physical size of this slug of carrier solution.

Each following slug of carrier solution comes into contact with a lower and lower concentration of sample and the sample is washed out relatively quickly (see Figure 7). Using the aqueous loop, washout was reduced to 20 s, which is a significant improvement on both the standard sample introduction system and the *ASXPRESS PLUS* system without a segmented carrier stream. Using an oils loop, similar profiles were obtained for the uptake and washout with an uptake delay of 20 s, a stabilization delay of 5 s, a sampling time of 196 s and a washout time of 16 s.

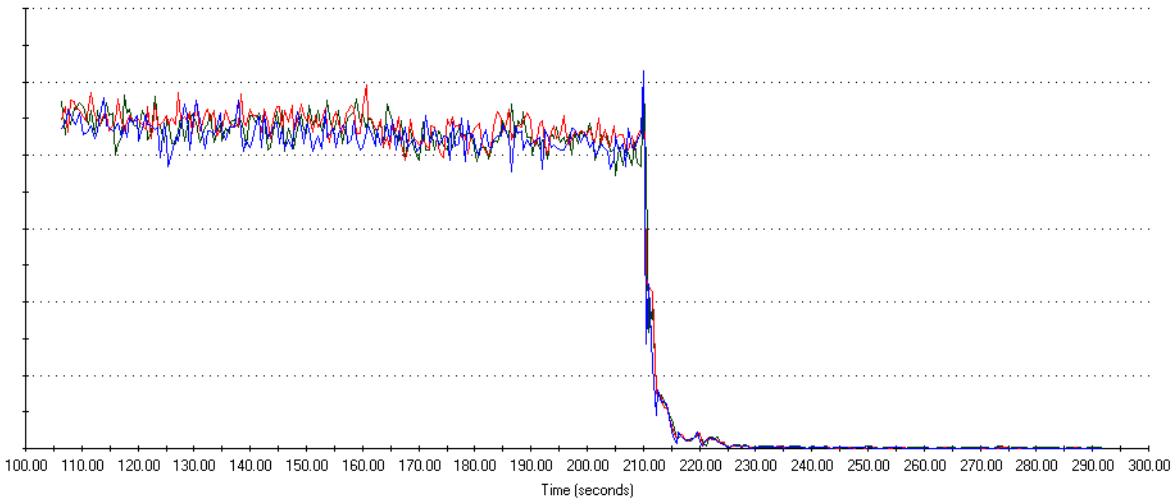

Figure 7 – Washout profile of 10 ppb tuning solution using the *ASXPRESS PLUS* system configured with an aqueous switching valve and a 1.02 ml aqueous sample loop using a segmented carrier stream pumped at ~300 µl min^{-1}

The segmented washout mechanism is more apparent using an 'oils' switching valve (with a 0.030" port diameter, instead of the 0.060" aqueous valve port size) and an aqueous sample loop (see Figure 8 below). There is an obvious 'step' down in the sample concentration as subsequent carrier solution slugs pass into the ICP. With the OV-AL combination, the first bubble is more pronounced but overall washout occurs ~10 seconds faster than with the AV-AL combination.

Figure 8 – Washout profile of 10 ppb tuning solution using the ASXPRESS PLUS system configured with an oils switching valve and a 1.02 ml aqueous sample loop using a segmented carrier stream pumped at ~300 µl min^{-1}

The timings for the different phases of the transient signal obtained from the tuning solution for all configurations are summarized in Table 2 below.

Table 2 – Method phase timings for sample introduction configurations on a Thermo Scientific X-Series II quadrupole Mass Spectrometer.[1]

Configuration	Sample Uptake Delay (s)	Stabilization Time (s)	Sampling Time (s)	Washout Time (s)	Total Time (s)	Sampling Efficiency[2] (%)
Standard	95	10	(200)[3]	105	410	48.7
AV-AL-CCS	11	35	85	340	471	18.0
AV-OL-CCS	11	30	95	230	366	26.0
AV-AL-SCS	20	7	183	20	230	79.6
AV-OL-SCS	20	5	195	15	235	83.0
OV-AL-CCS	11	29	132	198	370	35.7
OV-OL-CCS	10	29	85	145	270	31.4
OV-AL-SCS	18	7	165	35	225	75.0
OV-OL-SCS	19	5	203	18	245	82.9

From the table, it is apparent that the most efficient use of time in the method can be obtained by using a segmented carrier stream and a thin sample loop. The optimal combination appears to be using the 'Oils' switching valve with the 'Oils' sample loop and a segmented carrier stream, affording both the longest total sampling time (i.e., minimum diffusion) and the most efficient use of time in the method.

However, cavitation of the fluid on sample uptake has to be considered to avoid generating bubbles using high vacuum uptake. Reducing the inner diameter of the sample loop increases the probability of cavitation at a given flow-rate, since the linear velocity of the sample increases (and hence, the rate of frictional heating increases), converting more of the sample into the vapor phase.

CONCLUSION AND FURTHER WORK

This note has demonstrated that using a segmented carrier stream, created by introducing bubbles of air, has a beneficial effect on sample washout. Introducing bubbles speeds up washout by physically minimizing the extent of diffusion upstream relative to carrier stream flow.

Upstream diffusion is also minimized by reducing the inner diameter of the tubing used for the sample loop, as shown both experimentally and by numerical simulation. However; if the sample tubing is too small, frictional heating and cavitation processes will dominate, introducing bubbles into the sample stream that would have a detrimental effect on method precision.

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[1] AV = Aqueous Switching Valve (port diameter of 0.060"); OV = Oils Switching Valve (port diameter of 0.030"); AL = Aqueous Loop (i.d. ~2.5 mm); OL = Oils Loop (i.d. ~1 mm); CCS = Contiguous Carrier stream (pumped at ~300 µl min^{-1}); SCS = Segmented Carrier Stream (pumped at ~300 µl min^{-1})

[2] The sampling time as a percentage of the total time for all phases

[3] Calculated from 1.02 ml pumped at ~300 µl min^{-1} for comparison, assuming minimal diffusion

* EzyFit is a product of Glass Expansion