GLASS EXPANSION
Quality By Design

APPLICATION SPOTLIGHT

CHARACTERIZATION OF A CUSTOMIZED VALVE FOR ENHANCED PRODUCTIVITY ICP[1]

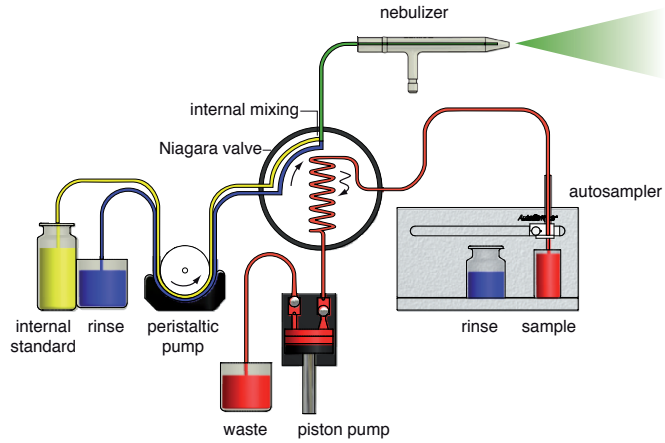

Fig. 1 a: Flow diagram for Niagara Plus a) filling sample loop, rinsing nebulizer and spray chamber (see overleaf for Fig 1 b).

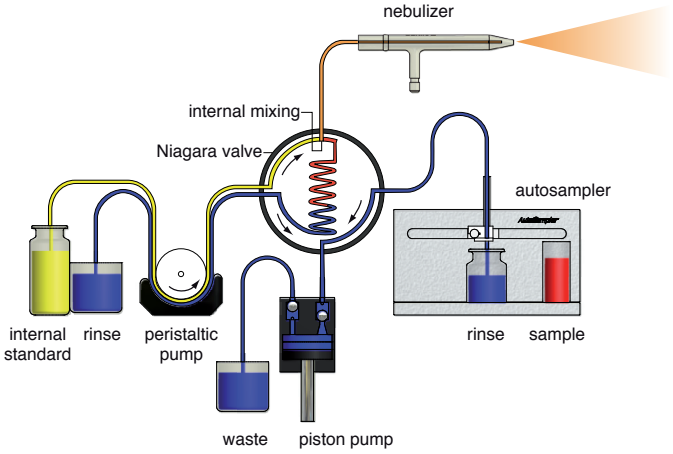

Fig. 1 b: Injecting sample, rinsing autosampler probe and sample line.

Introduction

Flow injection (FI) is not new; it was first described in the literature in 1975 (1). Flow Injection Atomic Spectrometry was first described in 1979 and since then numerous papers using FI with a variety of atomic spectrometry detectors have been published. A good review of these was published in 1997 (2). Early on, FI was used primarily with single analyte techniques such as flame AAS, cold vapor AAS and hydride generation AAS. More recently, with the maturation of multi-element techniques, it has been applied to ICP-OES and ICP-MS. The heart of the FI system is the switching valve that controls the flow of sample and rinse. Figure 1a and 1b shows the two positions of such a valve. In routine use with ICP techniques, the valve is switched back and forth many times per hour and in our opinion has become the weak link in the process. Therefore, Glass Expansion engineers, after searching in vain for an adequate "off-the-shelf" valve, have developed a valve customized for this process.

Characteristics

After working with these types of switching valves for over ten years, we developed a list of characteristics which were desirable in the new valve and these are listed below:

- Minimum swept volume - The swept volume is the volume inside the valve from the inlet to the exit. The smaller the swept volume, the faster the washout.
- Minimum distance from nebulizer - It is important to position the valve as close to the nebulizer as possible and to use a minimum swept volume connector to minimize carryover.
- Constant path internal diameter (ID) - We have found that it is best to keep the ID of the sample channel constant from the autosampler sipper probe to the nebulizer for minimum carryover. As Figure 2 shows, going from a small ID to a larger ID often leads to turbulence and dead volume, which lengthen washout. In fact, if an ID change is required, it is best to go from a larger ID to a smaller ID.
- Rigid rotor - The rotor is the component of the valve which turns inside the stator to direct the flow of solution. In the past, rotors made of Teflon were too soft and scored easily due to the presence of particulates in the sample, rendering the valve leaky and useless. For the sake of ruggedness, a hard material is preferable.
- Removable stator - The stator is the valve component in which the rotor moves. Either the rotor or the stator must be malleable enough to form a good seal. If the rotor is rigid, then the stator cannot be. It should also be easily accessed for maintenance or replacement.
- Built-in mixing tee - For ICP-OES, and especially for ICP-MS, the addition of internal standards is essential to achieve good accuracy, and an in-line approach greatly facilitates this process.
- Easy to configure - It is desirable to design a valve which facilitates the proper connection of the tubing to each of the ports.

The valve that we designed is shown in Figure 3. The rotor is made from rigid PEEK and the removable stator is made of Teflon. A low-volume mixing tee is built into the stator. Tests showed that washout and equilibration could be

1. Adapted from paper #*M07* presented at the 'Winter Conference on Plasma Spectrochemistry', January 4, 2010, in Fort Myers, Florida; authored by Jerry Dulude, Vesna Dolic and Scott Bridger.

accomplished with this design in 12 seconds compared to 44 seconds with an external mixing tee. The ports of the valve are color coded as are the included capillary tubing segments for easy assembly.

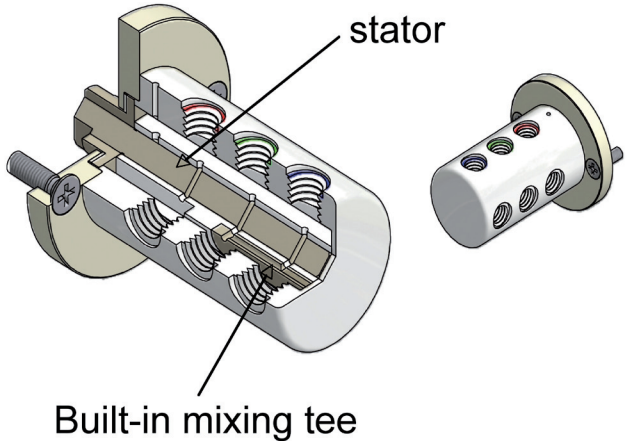

Fig. 3: Cutaway view of the purpose built valve.

For FI, in addition to the switching valve, a mechanism is needed for rapidly filling the sample loop and rinsing out the sample lines. The peristaltic pump of the spectrometer could be used for this purpose but it is too slow for the purposes of a high productivity system. Also, it is desirable to avoid contact of the sample with the peristaltic pump tubing to mitigate potential contamination and washout time. For these reasons, we chose a programmable positive displacement pump to perform this function. The system, consisting of the switching valve and the positive displacement pump, is shown in Figure 4.

Operation

The Niagara Plus system is controlled by a proprietary software application that runs in the background on the spectrometer PC. The software consists of 3 parts, SETUP screen, method wizard, and help files. The setup screen is shown in Figure 5. The standby tab allows the operator to select how and when the unit goes into hibernation mode due to inactivity and the communication tab is used to connect the appropriate communication ports. Some explanation of the fields on the SETUP screen is warranted.

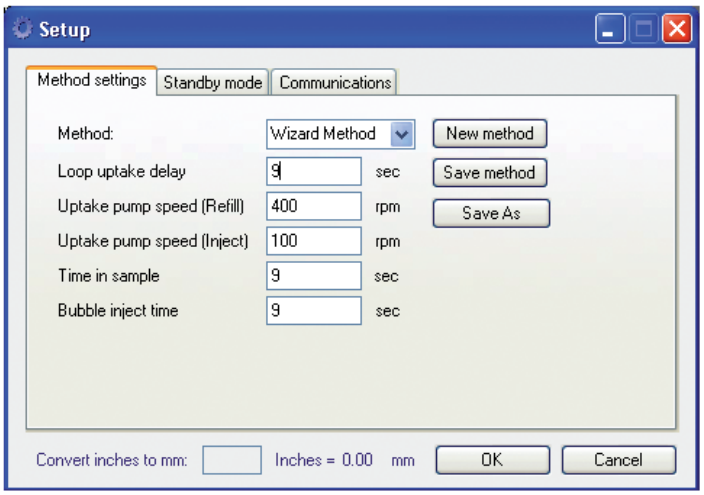

Fig. 5: Setup screen of the Niagara Plus software application.

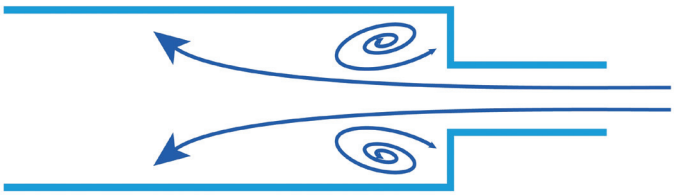

Fig. 2: Illustration of turbulence and eddy effects caused by increasing the internal diameter of the sample path

Fig. 4: Photo of the Niagara Plus system consisting of the switching valve in the front and the positive displacement pump at the rear.

- Method: methods created and saved using the method wizard can be recalled from memory
- Loop Uptake Delay: This is the amount of time that the sample loop is being filled via the positive displacement pump
- Uptake pump speed (refill): This is the speed of the positive displacement pump during the filling of the sample loop in rpm.
- Uptake pump speed (inject): This is the speed of the pump in rpm during the stage where the sample loop is being injected into the nebulizer and the sample lines are being rinsed. This may be a relatively long time period as this is when analyte measurement takes place (typically 30 to 60 seconds). For this reason, you may not want to generate a large volume of waste and consume a large volume of rinse and therefore a lower speed can be used.
- Time in Sample: This field is used to determine when the autosampler probe moves from the sample. Since the sample line is full, there is no need for the autosampler probe to stay in the sample during the entire Loop Uptake Delay. Reducing this time further reduces the analytical cycle and in addition reduces the volume of sample consumed.
- Bubble Inject Time: The software provides the option to inject a series of air bubbles at the end of the sample segment. This provides a barrier to sample boundary diffusion and thus reduces the amount of sample (and time) required to accurately and consistently fill the sample loop.

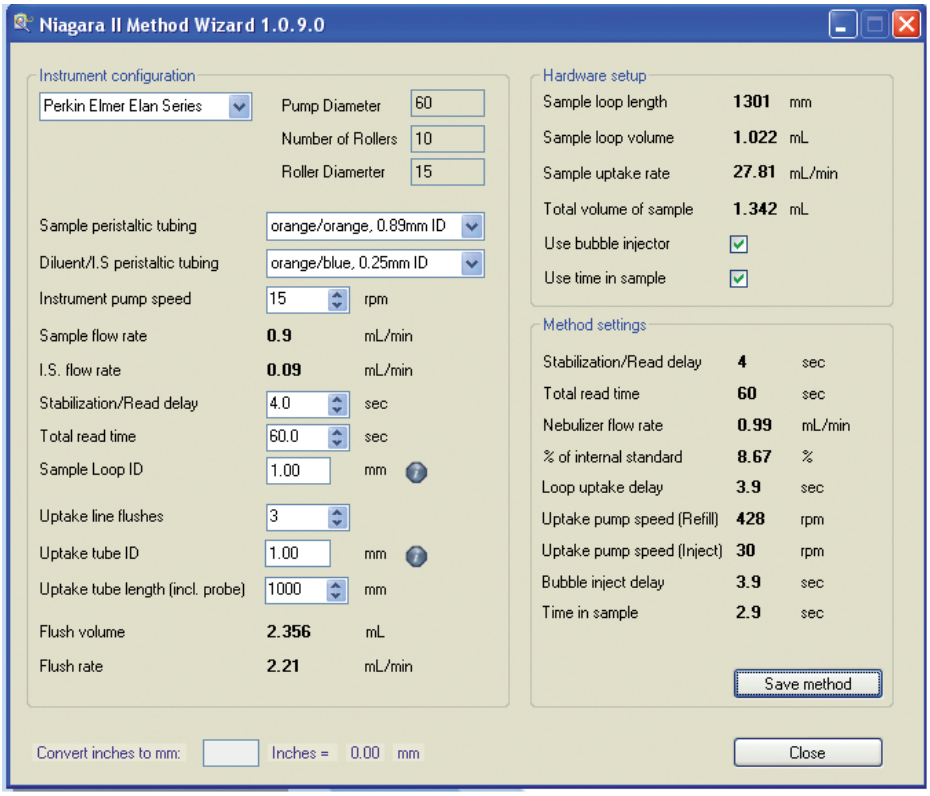

Fig. 6: Method Wizard screen of the Niagara Plus software application.

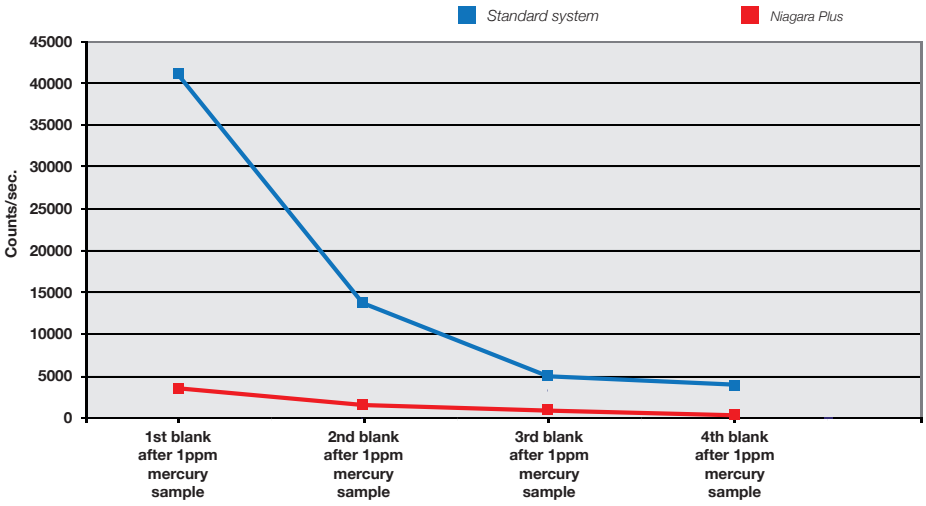

Fig. 7: Comparison of carryover with and without the Niagara Plus.

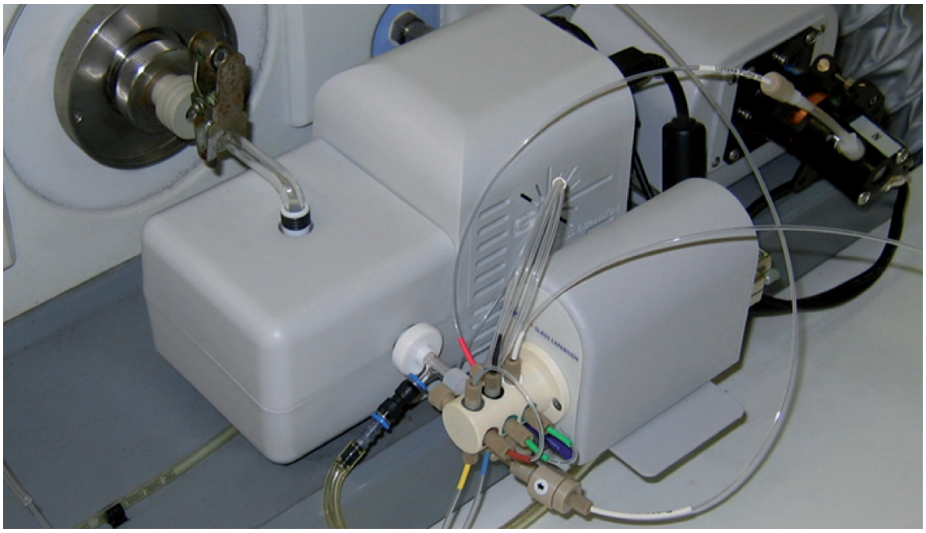

Fig. 8: Photo of Niagara Plus integrated with an IsoMist Programmable Temperature Spray Chamber and installed on an Elan 9000 ICP-MS.

Instrument parameters

- RF power: 1400 W
- Nebulizer gas: 0.89 L/min
- Make-up gas: 0.13 L/min
- Pump speed: 0.21 rps
- Spray chamber temperature: 2°C

Table I: Agilent 7500 conditions

	Standard system	Niagara Plus
	Sec	Sec
Uptake time	170	6
Stabilization	60	15
Rinse	120	0
Read time	111	111
TOTAL	7 min, 41 sec	2 min, 12 sec

Table II: Comparison of sample cycle times on Agilent 7500

The method wizard is shown in Figure 6. The fields with drop down arrows are editable while the other fields simply show the effects of making changes to the editable fields. Once the operator is happy with the outcome of the settings, the method can be saved for future recall.

Performance

There are a number of potential advantages to using this type of enhanced productivity device. Most obvious is the increase in productivity resulting from the reduction in sample cycle time. But there should also be an improvement in washout due to the fact the sample comes in contact with the sample introduction components for less time. In fact, with the system described here, the sample does not come in contact with the peristaltic pump tubing at all, which otherwise could be a source of carryover. For the same reasons, memory effects should be lessened as well. A final benefit is the extended life of consumables due to reduced sample wear.

We used an Agilent 7500 to examine carryover using standard conditions as described in Table I. Table II shows the comparison of stage times for the method with and without the Niagara Plus. Figure 7 compares carryover with and without the Niagara Plus system for mercury using only a 0.5% HNO_3 rinse solution. You can see that even using a 120 second rinse with the standard system, significant carryover is seen,

Mass	% recovery	
	w/o Niagara Plus	w/ Niagara Plus
Be9	117	95
Al27	119	98
Ti47	106	105
Ti49	113	103
V51	119	103
Cr52	121	102
Cr53	112	101
Mn55	114	111
Co59	141	103
Ni60	146	104
Ni62	150	100
Cu63	149	108
Cu65	149	108
Zn66	133	102
Zn67	134	100
Zn68	117	101
As75	100	104
Se77	90	108
Se82	94	101
Sr88	104	100
Mo98	102	
Ag107	101	83
Cd111	98	101
Cd114	100	101
Sn118	102	100
Sb121	103	102
Ba137	97	99
Tl205	108	104
Pb208	110	101

Table III: Memory effects on calibration check

while with the Niagara Plus, carryover is dramatically reduced despite elimination of the programmed rinse. Of particular interest is the reduction in sample analysis time achieved; from seven minutes and 41 seconds to two minutes and 12 seconds. To put this in perspective, of the 132 seconds consumed for the sample cycle, 111 or 84% is spent accumulating data and only 21 seconds or 16% is spent on overhead. The instrument is producing data 84% of the time instead of 24% without the Niagara Plus.

We also looked at memory effects on an Elan 9000 at a customer's site. One of the reasons for adding the Niagara Plus was hopefully to facilitate the analysis of a recurring batch of troublesome samples. Severe memory interferences would cause the QC checks to fail and require multiple analyses and sometimes dilutions before results could be reported with confidence. In this case, (see Figure 8) a Niagara Plus was integrated with an IsoMist Programmable Temperature Spray Chamber. (Previously the chamber was operated at ambient temperature.) Table III shows the results of a QC check following this batch of samples. Note that more than 50% of the masses fell outside the 10% acceptable range in standard mode, but all but 2 passed when the Niagara Plus was used. Although, the data in Table III appears to show an enhancement, it was actually a suppression of the internal standard masses that led to the errant results (Table IV), a suppression which disappears with the Niagara Plus. The salient parameters are given in Table V. Note that the analyst was able to halve the number of sweeps/amu and maintain the same level of precision, an improvement that he attributed to the lowering and stabilization of the spray chamber temperature. This reduction of sweeps halved the necessary analyte measurement time. The lower temperature resulted in a higher optimum nebulizer gas flow rate which improved sensitivity, especially for the low mass analytes. Thus, he was able to reduce the method cycle time from four minutes and 30 seconds to one minute and 20 seconds.

Mass	w/o Niagara Plus	w/ Niagara Plus
Li6	45	110
Sc45	50	115
Y89	49	109
In115	53	105
Tb159	63	104

Table IV: Memory effects on QC (internal standards)

Consumables expenses are also reduced. In the case of the Elan user, a tank of argon lasted through four times as many samples as previously. Similar savings are to be realized due to the reduction in wear on nebulizers, torches, and interface cones.

Parameter	w/o Niagara Plus	w/ Niagara Plus & IsoMist (3°C)
Sweeps/amu	16	8
Analysis	120 sec	60 sec
Load/ stabilization	30 sec	7 sec
Read delay	30 sec	8 sec
Rinse	100 sec	0 sec
Neb argon flow	0.92 L/min	0.98 L/min
Analysis time	4 min, 30 sec	1 min, 20 sec

Table V: Environmental method on Elan 9000 under standard conditions

Conclusion

After many years of testing, we believe we have developed a second generation switching valve customized for use with FI. It is more robust and shows the least carryover and fastest washout of any valve we have tested. Because of the decreased memory effects and extended lifetime of consumables, we believe the Niagara Plus not only dramatically enhances productivity, but also, and perhaps more importantly for laboratories without high sample loads, increases the robustness of ICP-OES and ICP-MS instrumentation.

Acknowledgements

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References

1. Ruzicka, J. and Hansen, E.H., *Anal. Chim. Acta*, **78**, 145 (1975).
2. Burguera, J.L. and Burguera, M., J. *Anal. At. Spectrom.*, **12**, 643 (1997).