Technical Note 144

Inline Filtration for Ion Chromatography

Bernard Sheldon, Thermo Fisher Scientific, Sunnyvale, CA, USA

Key Words
Carry Over, Filtration, Installation, Particulates, Setup

Goal

Demonstrate the utility, installation and operation of several approaches to inline filtration available to ion chromatography (IC) system users.

Introduction

Filtration can be used to remove contaminating microbes from samples; microbes can change the sample composition by metabolizing select constituents (for example nitrate, nitrite, orthophosphate, and perchlorate[1]). Filtration for the purpose of sample stabilization should be performed at or immediately after sample collection, and is required by some official methods (ISO 5667-3[2], EPA 314.1[3])

Filtration also serves to remove particulate contamination from samples before injection into a chromatography system.[4] This helps preserve column lifetime and performance. Some samples, particularly those high in iron, can form precipitates during storage even after an initial filtration, so a secondary filtration immediately before injection is useful in this case. Inline filtration is inherently automated, making the filtration process simple, reliable, reproducible and inexpensive.

Complicating factors for filtration include unpredictable clogging of filters as well as potential sample carry over. The inline filtration approaches discussed here help alleviate these issues.

Equipment

Thermo Fisher Scientific offers two primary, complementary and markedly different approaches to inline filtration. The first is the use of the Thermo Scientific™ Dionex™ AS-DV Autosampler with dedicated vials and individual filter caps. The second is the use of inline high-pressure filters. Both of these methods are completely automated, offering all the advantages listed above.

Dionex AS-DV Autosampler and Filter Caps

The Dionex AS-DV Autosampler filter cap technique is illustrated in Figure 1. A sample is dispensed into an inert sample vial and a plunger cap with an integral filter is installed in the top of the vial (caps without filters are available for samples not requiring filtration). The autosampler arm applies a sampling tube which forms a hermetic seal with the filter cap and which then pushes the cap into the vial, displacing sample upwards through the filter. Filtered sample is transferred hydraulically to the injection valve loop, or to a concentrator column.

Figure 1. Dionex AS-DV Autosampler sample displacement filtration.

The Dionex AS-DV Autosampler filtration approach is amenable for a wide range of samples, including those which are heavily loaded with particulates. Filtration occurs from the top down, so filtration efficiency is assisted by gravity which acts to deposit larger particles in the bottom of the tube; thus, the filter acts on the least contaminated part of the sample. The filter frit in the Dionex AS-DV Autosampler filter cap comprises a large cross-section and large volume, increasing its capacity. Each sample has its own individual filter, eliminating sample carry over related to the filter. The sample is filtered before coming into contact with any of the instrument plumbing, thus improving system reliability. The autosampler is mechanically very robust, using a simple and rugged mechanism for sample displacement and filtration. The basic filtration approach using displacement has been proven by decades of use in various autosamplers.

Figure 2. Filter cap inserted into the Dionex AS-DV Autosampler vial. Note heavy sedimentation.

Figure 3. (a) Unused and (b) used filter caps.

Figure 4. Clarified sample post-filtration.

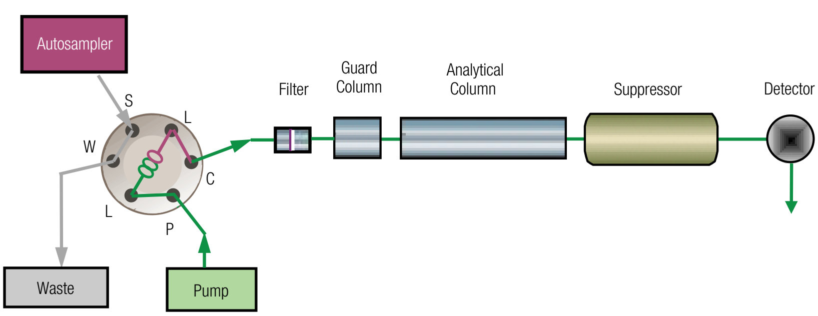


Figure 5. Inline high-pressure filtration schematic.

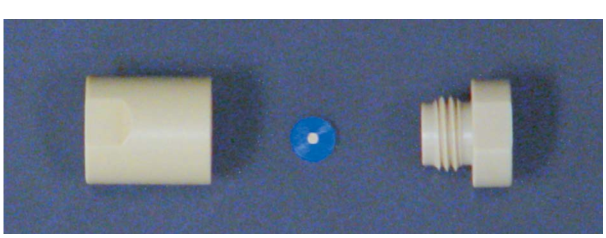


Figure 6. Inline high-pressure filter assembly.

Inline Low Volume, High-Pressure Filter

The inline high-pressure filter plumbing schematic is shown in Figure 5, and assembly is shown in Figure 6.

The low volume filter is placed in the high-pressure flow path of the ion chromatograph, after the injection valve. The filter in this location serves to remove particulates from the sample and protects the guard column from clogging due to particulate accumulation in the inlet frit of the column. The inline filter frit cross-section is narrow and the frit thickness proportionate to the surface area, so the dead volume in the frit is very low, less than 1.5 µL. The low dispersion volume permits filtration of just the injected sample volume, generally 10 to 25 µL, without significant band broadening effects. The small sample volume filtered enhances filter media lifetime. This approach is not recommended for highly contaminated samples, for which the Dionex AS-DV Autosampler filter caps previously described are better suited.

Inline filtration installed on the high-pressure side of the injection valve provides two major benefits:

- The filter is constantly exposed to eluent flow so sample carry over is essentially eliminated
- System pressure can be used to monitor filter condition

The second advantage depends on the ability of the chromatography instrument to monitor system pressure, a feature all Thermo Scientific Dionex IC systems are capable of. The system pressure is continuously monitored and recorded by the chromatography data system. Monitoring system pressure allows the user to ascertain when the time has come to service the filter. Increased system pressure implies that the filter frit is loading up with particulates and needs to be changed. A good rule of thumb is to change the frit when the system pressure has increased by 10 to 20%. Use of the IC pressure limit feature makes this very convenient – a user would observe the system pressure when the filter frit is newly installed. The pressure limit would then be set to 20% higher than this typical operating pressure. When this pressure is reached the system can be programmed to warn the operator.

Maintenance of the inline filter is very simple – one of the tubing connectors is removed, allowing that half of the filter housing to be unscrewed. The filter frit is replaced, the housing is screwed back together, and the tubing reinstalled. The system is ready for operation in minutes.

Dual Inline Filter Frits with Back Flush

A filter back flush approach can be implemented where particulate loading of samples is heavier or concerns about sample carry over remain. As shown in Figure 7 the plumbing scheme for this requires a secondary 2 position 10-port high pressure valve. The Thermo Scientific Dionex ICS-1100, 1600 or 2100 integrated IC systems, can be easily equipped with an integrated auxiliary valve. The modular Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system can also be setup in this way.

Two filters are installed on the auxiliary valve (as shown in Figure 7, Filter 1 and Filter 2), along with a Thermo Scientific Dionex AXP auxiliary pump or other high-pressure pump (one pump of a dual channel Dionex ICS-5000+ DP pumping system could also be used). The Dionex AXP pump is capable of producing high flows and pressures with precise flow rate control and is an economical choice for back flush applications. (It is recommended that enough back pressure tubing be added just after the Dionex AXP pump and before the valve to produce a back pressure of at least 1000 psi at the desired flow rate.) When plumbed as illustrated, back flush flow traverses the filter frit in the direction opposite to the sample introduction, so particulates are flushed off the frit to waste. This dramatically extends filter lifetimes. As an example, in one application, filters without back flush clogged after 7 injections; with back flush, a thousand injections were experienced without clogging. The chromatogram overlay in Figure 8 demonstrates that the filtration/back flushing process has no impact on chromatography after several dozen (n = 66) sample injections.

Consistent chromatographic performance is further demonstrated by retention time stability, in Figure 9. The retention time stability over a series of 100 successive sample injections yielded 0.11% RSD. The effectiveness of the filtration back flush process can be seen by observing the system pressure over a series of injections, as shown plotted in Figure 10, where system pressure increased over a series of 50 injections by only about 10 psi, about 0.5%. This very small increase in back pressure indicates that the back flush process is very effective at cleaning the filter of particulates. A secondary method for monitoring filter effectiveness is to observe the pressure of the back flushing stream. A low and stable pressure demonstrates once again that the filter is not clogging with particulates. This can be seen in a plot of the pressure of the pump used for the back flushing against the number of injections as shown in Figure 11.

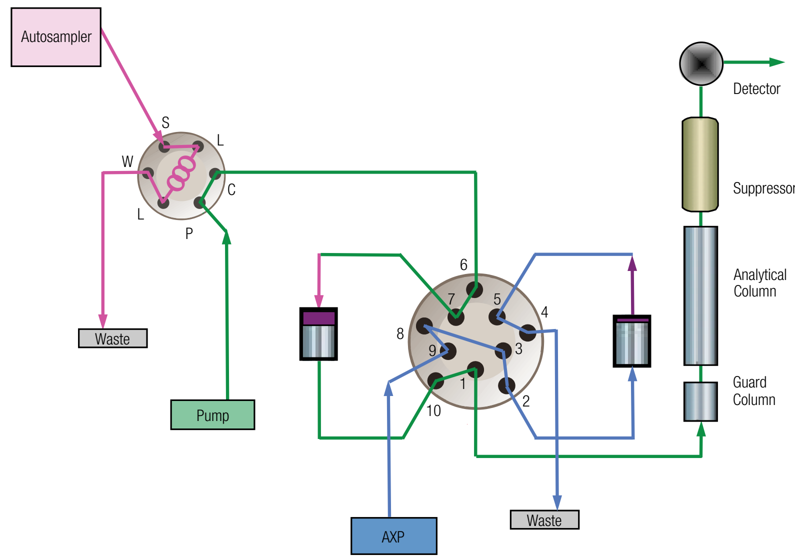


Figure 7. Inline high-pressure filtration schematic, dual filter with back flush.

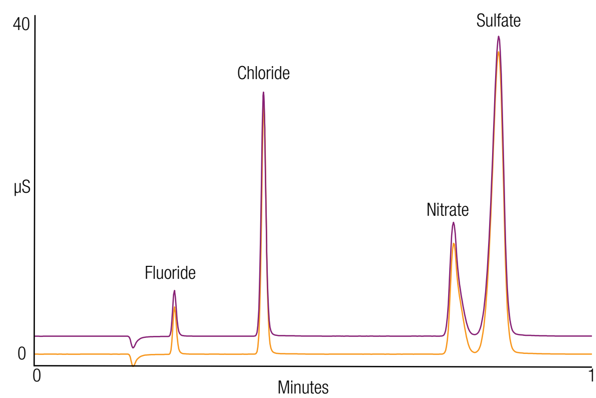


Figure 8. Sample overlay of the first and 66th injections demonstrates excellent retention time stability.

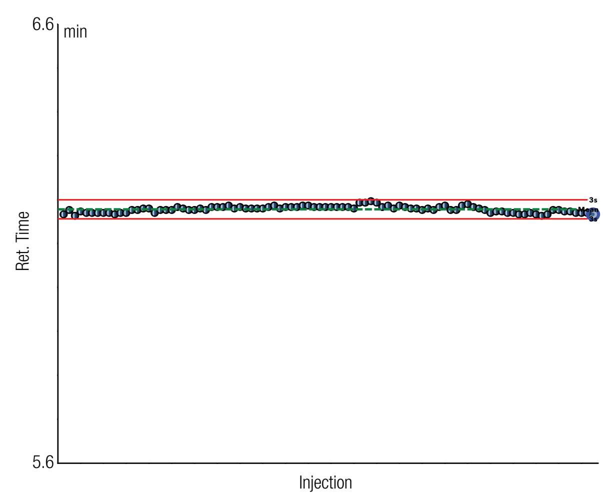


Figure 9. Chloride retention time, consecutive injections. RSD ~0.11%.

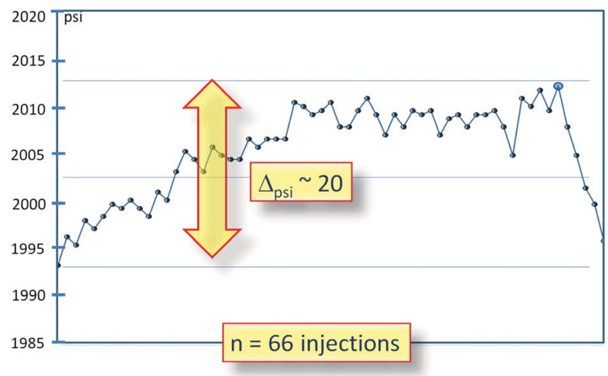


Figure 10. Plot of system pressure, consecutive injections, Δ_{psi} ~20.

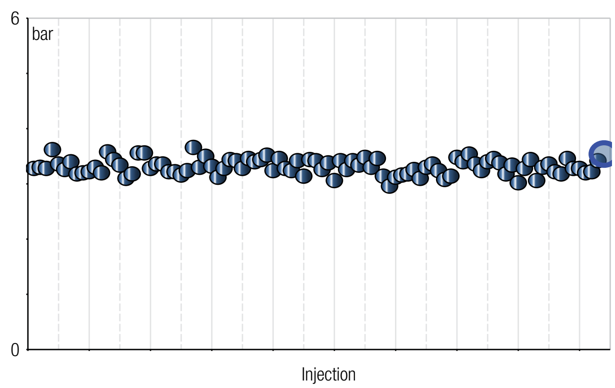


Figure 11. Plot of back flush pressure for consecutive injections.

Method Programming for the Filter Back Flush

The analytical procedure requires that the 10-port valve mounting to the two filter cartridges change position for each injection, so that injections alternate between passage through filter cartridge A and B. This can be affected in a number of ways, two of which are described here and shown in detail in the Appendix to this document.

Approach 1: a User Contributed Column is added to the sequence table which specifies the valve position. The variable "A" or "B" is specified in this custom column and selects the position the 10-port valve should be in. The valve position parameter is switched after each injection and alternated through the length of the sequence so that alternate filters are used and back flushed.

Approach 2: a pair of Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software instrument control programs can be created to alternate between the two inline filters and manage the back flush. Name the programs identically except for the valve position designation A or B and alternate them in the sequence file. The flow rate for the pump used for flushing the filter can be determined by observing the back pressure across the filter – typically the flow will be from about ½ to 1 times the analytical flow rate.

Table 1. Filtration part numbers.

Dionex AS-DV Autosampler Displacement Filtration	
Description	Part Number
Dionex AS-DV Autosampler for 5 mL vials	068907
Dionex AS-DV Autosampler with adapters for 0.5 mL vials	068908
5 mL vials and filter caps, box of 250	038141
0.5 mL vials and filter caps, box of 250	038142
Filter caps for 5 mL vials, box of 250	038009
Filter caps for 0.5 mL vials, box of 250	038011
Inline High-Pressure Filtration	
Description	Part Number
Inline high-pressure, low volume, kit, 0.5 µm PEEK frits	074505
Replacement frits, 0.5 µm PEEK, pack of 5	074506
2 position, 10-port auxiliary valve; Dionex ICS-1100/1600/2100	071589
2 position, 10-port auxiliary valve; Dionex ICS-3000/5000/5000+	075918
Dionex AXP auxiliary pump	063973

References

1. Xu, J., Y. Song, B. Min, L. Steinberg, and B.E. Logan. 2003. Microbial degradation of perchlorate: principles and applications. *Environ. Engin. Sci*, 20(5): 405-422.
2. ISO 5667-3, Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples. http://www.iso.org/iso/catalogue_detail.htm?csnumber=33486
3. Wagner HP, Pepich BV, Pohl C, Later D, Joyce R, Srinivasan K, Thomas D, Woodruff A, DeBorba B, Munch DJ. *J Chromatogr A*. 2006 Jun 16;1118(1):85-93. Epub 2006 Mar 10.
4. ISO 10304-1, Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate. http://www.iso.org/iso/catalogue_detail.htm?csnumber=46004

Appendix – Chromeleon 7.2 CDS Programming

A. Custom Column in Sequence Table

A custom column can be added to the sequence table to specify the position of the auxiliary valve, and thus the filter to be used (the alternate filter will be flushed during the analysis).

In the column header area of the Sequence table, right click and choose “Custom Columns”. From the submenu, select “Insert Custom Injection Column”, as shown in Figure 12.

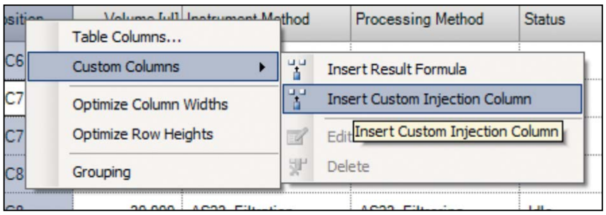


Figure 12. Adding a custom column to the Sequence Table, Chromeleon 7.2 CDS.

In the new pop up window select “Create new custom variable” and press “Next”.

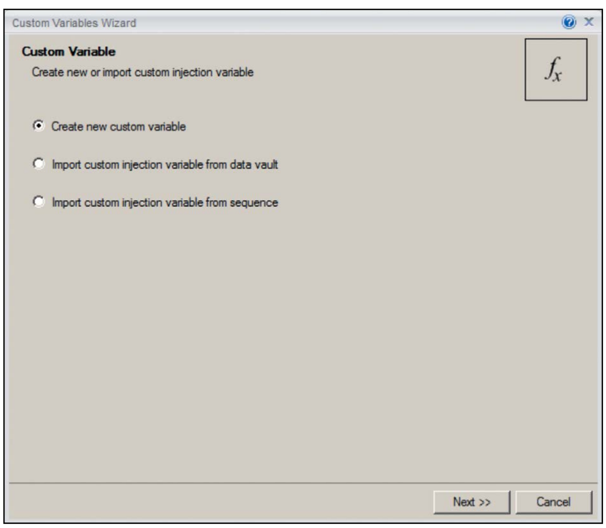


Figure 13. Custom Variable Wizard, Page 1.

Enter the desired name of the variable (note that the software does not read spaces, so underscores must be used instead if you choose to use more than one word.) Click Finish.

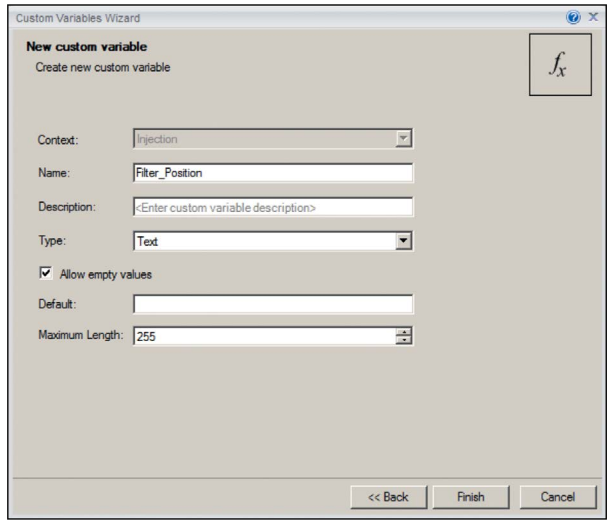
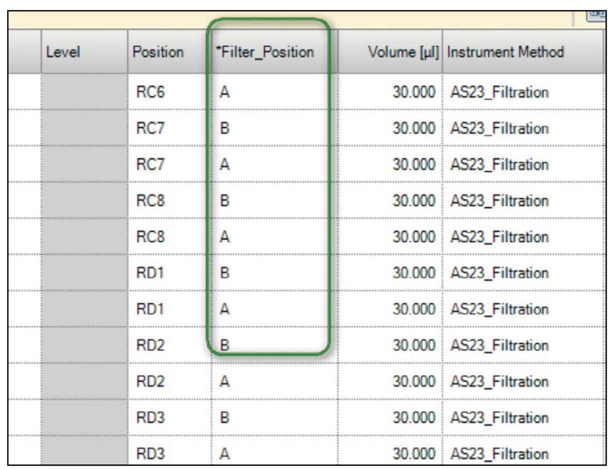


Figure 14. Custom Variable Wizard, Page 2.

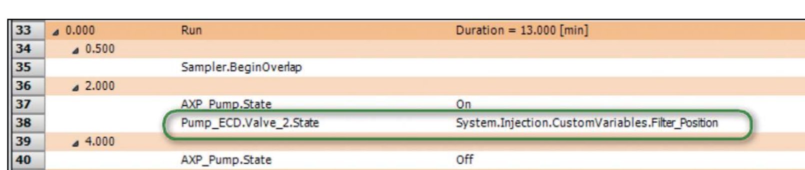
You will now have a new column in the Sequence Table, in which you can designate the valve position, in this case alternating between the two positions and thus the two filters and the back flush pump.



Level	Position	*Filter_Position	Volume [µl]	Instrument Method
	RC6	A	30.000	AS23_Filtration
	RC7	B	30.000	AS23_Filtration
	RC7	A	30.000	AS23_Filtration
	RC8	B	30.000	AS23_Filtration
	RC8	A	30.000	AS23_Filtration
	RD1	B	30.000	AS23_Filtration
	RD1	A	30.000	AS23_Filtration
	RD2	B	30.000	AS23_Filtration
	RD2	A	30.000	AS23_Filtration
	RD3	B	30.000	AS23_Filtration
	RD3	A	30.000	AS23_Filtration

Figure 15. Sequence Table with new custom column showing the valve position variable, A or B.

Go to the Instrument Program you wish to use, and select the command that you want to link the custom column to. In this case it will be *Pump_ECD.Valve_2.State*. To do this, add the custom variable designator to the Value section after the command. The custom variable designator is *System.Injection.CustomVariables*. This is followed by the name of the variable, in this case *Filter_Position*, which was inscribed in the New Custom Variable window previously.



33	0.000	Run	Duration = 13.000 [min]
34	0.500		
35		Sampler.BeginOverlap	
36	2.000		
37		AXP_Pump.State	On
38		Pump_ECD.Valve_2.State	System.Injection.CustomVariables.Filter_Position
39	4.000		
40		AXP_Pump.State	Off
41	13.000	Stop Run	

Figure 16. Instrument control method, showing Custom Variable value associated with the “Valve Position State” command.

B. Two different Instrument Programs

Two nearly identical analytical programs are created, one with the auxiliary valve in position A, the other with the valve in position B. In the case of the Dionex ICS-1100/1600/2100 IC systems the command line would read *Pump_ECD.Valve_2.A* and *Pump_ECD.Valve_2.B* in the two programs, respectively. The valve position command would generally be placed at the beginning of the program. The two programs are named to identify which position of the valve the program calls. The programs are then alternated in the Sequence Table.

53		PumpModule.PumpLeft.%C.Value	0.0 [%]
54		PumpModule.PumpLeft.Curve	5
55	13.000		
56		Pump_ECD.Valve_2.B	
57	15.000		

Figure 17. Instrument control method, showing valve position command, selected for position B.

Position	Volume [µl]	Instrument Method	Processing Method
RA1	30.000	AS23_FiltreringA	AS23_Filtrering
RA1	30.000	AS23_FiltreringB	AS23_Filtrering
RA1	30.000	AS23_FiltreringA	AS23_Filtrering
RA1	30.000	AS23_FiltreringB	AS23_Filtrering
RA7	30.000	AS23_FiltreringA	AS23_Filtrering
RA7	30.000	AS23_FiltreringB	AS23_Filtrering
RA6	30.000	AS23_FiltreringA	AS23_Filtrering
RA6	30.000	AS23_FiltreringB	AS23_Filtrering
RA5	30.000	AS23_FiltreringA	AS23_Filtrering
RA5	30.000	AS23_FiltreringB	AS23_Filtrering

Figure 18. Sequence Table showing alternating instrument control programs.

www.thermofisher.com/dionex

TN70877_E 09/16M