

응용 자료

Hints and Tips for APGC Coupled with Xevo TQ-S for Food and Environmental Analysis

Adam Ladak, Lauren Mullin, Rhys Jones

Waters Corporation



This is an Application Brief and does not contain a detailed Experimental section.

Abstract

The powerful combination of Waters Xevo TQ-S equipped with APGC ionization provides a robust and highly sensitive analytical solution for the analysis of compounds at ultra-trace levels. Here, this document provides a guide for using APGC with Xevo TQ-S operating with MassLynx SCN 905 or later.

Benefits

The Xevo TQ-S APGC, equipped with the patented StepWave Technology enables detection limits at ultra-trace levels providing:

- Compliance with regulatory limits.
- Ability to inject less sample matrix, reducing effects of contamination on the GC system.
- High levels of matrix tolerance.
- Excellent injection to injection repeatability.
- Ability to switch between APGC and UPLC in under five minutes for expanded compound coverage.

Introduction

Ever tightening regulatory demands lead to greater sensitivity requirements from commonly used analytical techniques such as GC-MS. In addition, there is a desire to reduce the injected volume of samples in order to minimize matrix effects and the contamination of instrumentation. The powerful combination of Waters Xevo TQ-S equipped with APGC ionization provides a robust and highly sensitive analytical solution for the analysis of compounds at ultra-trace levels.

This document provides a guide for using APGC with Xevo TQ-S operating with MassLynx SCN 905 or later.

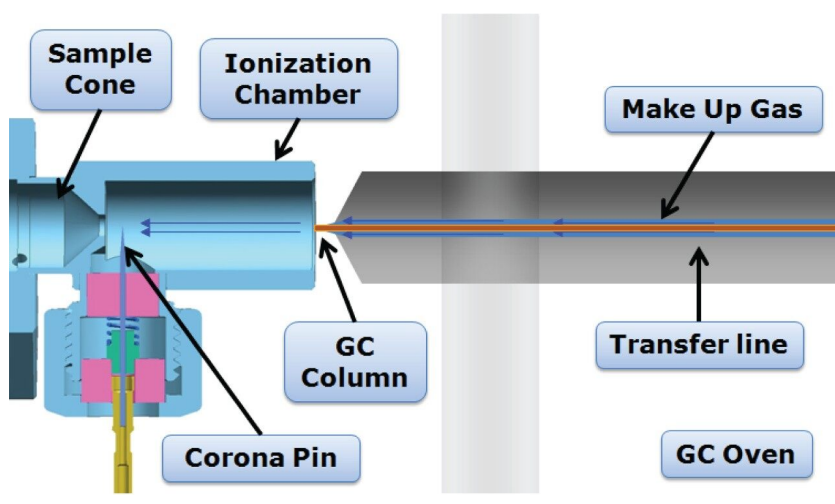


Figure 1. APGC components.

Experimental

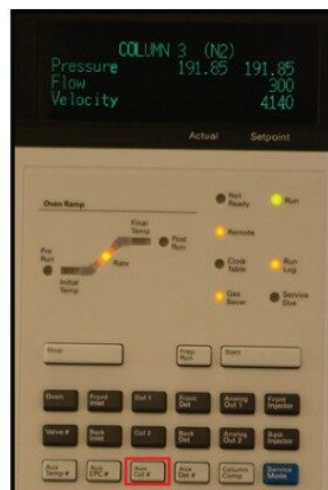
Setup

First install a GC column and injection liner that is suitable for your analysis. A J and W DB5 30 m x 0.25 mm x 0.25 μ m column is provided with the APGC. Ensure helium is flowing before increasing any temperatures on the GC. The nitrogen make up gas flows around column to sweep the ionization chamber and delivers heat to the tip of the column. This can be set using the GC keypad. First press Aux column and enter 3 when prompted to select a number. Next set the flow to 300 mL/min (Figure 2).

The transfer line temperature can be heated by selecting Aux temperature on the GC keypad (Figure 3). Normally this is set to 10 °C above the top oven temperature. If you do not have that information set it 10 °C below the maximum operating temperature of the column to ensure the column is not damaged. The column should be set in the transfer line with 1 mm of the column protruding from the end (Figure 4). The column should be set when the GC transfer line is at temperature to ensure correct placement.

Before installing the ionization chamber, set the corona pin between the exit of the ionization chamber and the cone orifice (Figure 5). This position has been found to give the best sensitivity for APGC in all ionization modes. The distance between the ionization chamber and the transfer line should be set to 1.2 mm (+/-0.2), as shown in Figure 6. This can be set by using an Allen key on the side of the GC which is hidden by a screw.

This is normally set on installation and does not need adjusting once set.



APGC Set Up Work Flow

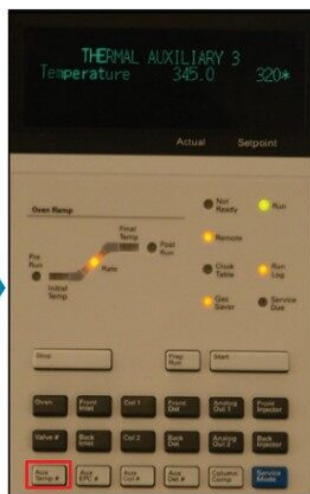


Figure 2. Set up of makeup gas.

Figure 3. Set up of transfer line temperature.

Figure 4. GC column set in transfer line.

Figure 5. Correct positioning of corona pin in ionization chamber

Figure 6. Positioning between the ionization chamber and the transfer line.

Note the position between the ionization chamber and the transfer line is set during install. It is included here for reference only and normally does not need adjusting.

Tune Page Setup

Corona current

This is the current that is applied to the tip of the corona for ionization of the analytes, which is generally set between 1 and 5 μA in APGC.

Sample cone

When applying voltage to the sample cone, the voltage has a wide optimization range between 10 and 80 volts. This is due to the large cone orifice on the Xevo TQ-S, meaning ions readily enter the system. Exceeding 80 volts may cause in source fragmentation.

Source offset

Ions flowing through the sample cone are pulled through the StepWave ion transfer device. The ions then enter into the analyzer region of the mass spectrometer. The source offset again has a large optimization range between 10 and 100 volts.

Cone gas (L/hr)

The nitrogen gas flow around the sample cone, which can be used to affect the flow of gases through the APGC ionization chamber. A typical value is between 150 and 250 L/hr.

Auxiliary gas (L/hr)

The nitrogen gas flow into the API source that sweeps around the source enclosure and has more of an effect when using a modifier in the source (typically 150 to 1000 L/h).

APGC+ Source		Fluidics		Advanced	
Source Fitted		ESI:1			
Voltages Mode ☒ Current ☐ Voltage					
Corona (uA)	0.0	2.0			
Cone (V)	-3	30			
Source Offset (V)	50				
Gas Flow					
Auxiliary(L/hr)	3	200			
Cone (L/hr)	2	200			
Nebuliser (Bar)	0.0	5.0			

Figure 7. Default tune settings for APGC.

To minimize reduction in the injection solvent front reproducibility, extra functionality has been added to MassLynx Software (v.SCN 905 and later). It is recommended to increase the corona voltage to 20 μ A, and turn the cone gas to 0 at 0 minutes, and during the solvent front. This allows for the solvent to dissipate the solvent more readily. This is managed using Method Events in the MS method (Figure 8). After the solvent front has passed, the settings can be returned to the normal values. If the first eluting compound is 15 minutes after the solvent front, the ionization will have time to eliminate the solvent under normal conditions and it is not necessary to use the method events.

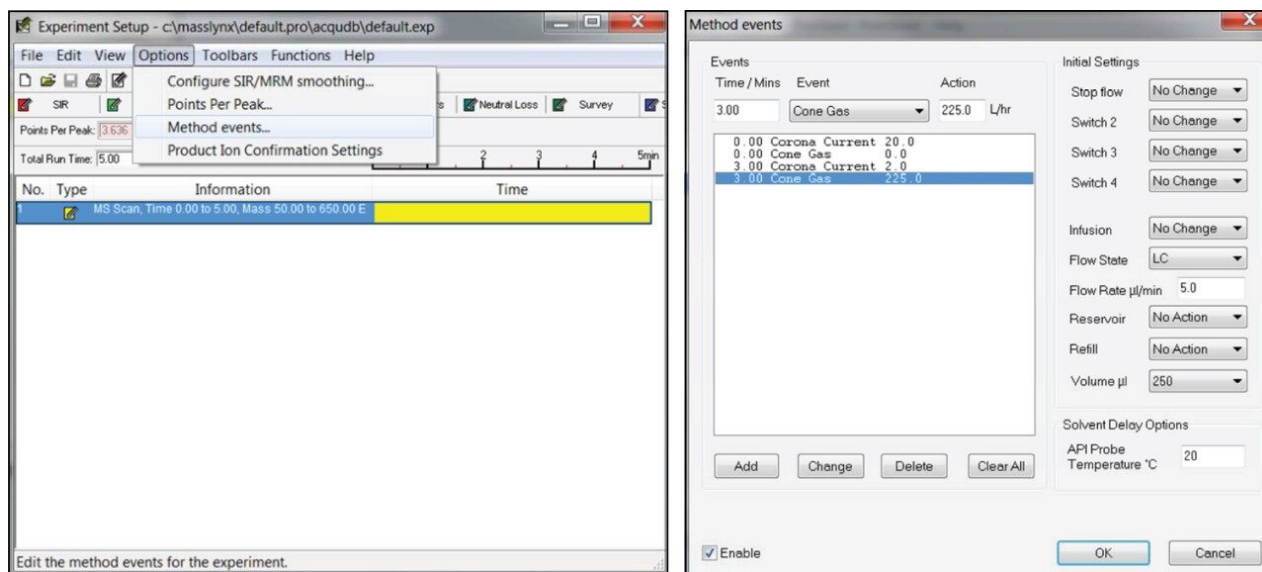


Figure 8. Setting up method effects to reduce injection solvent front effects.

Results and Discussion

There are a number of established optimized methods available from Waters using APGC and Xevo TQ-S. Table 1 lists the compound classes and the references for the optimized APGC methods available. These include the GC methods, MRM transitions, and source conditions.

If it is necessary to perform APGC optimization, experiments should be completed using a standard of 100 ppb. APGC can be operated under charge transfer or protonation conditions. For charge transfer, the source is kept dry to allow the mechanism to occur. In protonation, the source is doped with water, methanol, or IPA using the vial holder in the bottom of the source (Figure 9). A controlled mixed mode operation where both charge transfer and protonation occur together can also be utilized. The mechanism with the largest area response should be selected for the compound of interest.

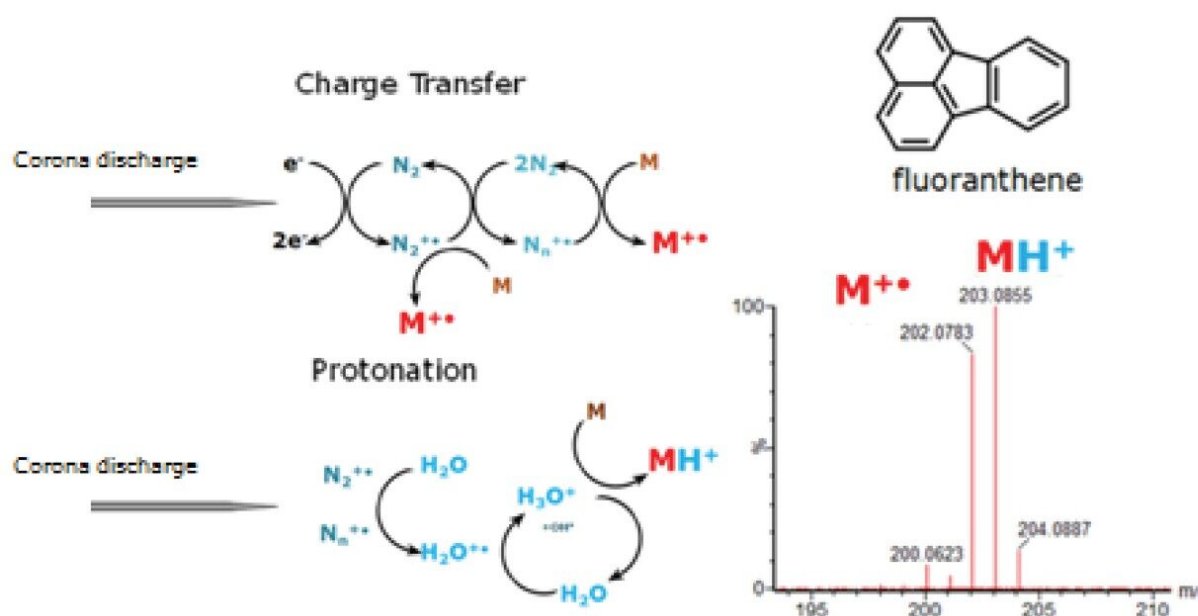


Figure 9. Selection of ionization mechanism with fluoranthene as an example.

The type of ionization mechanism to use depends on the compounds being analyzed. Table 1 shows common classes of compounds that are analyzed in food and environmental applications for which the ionization mechanism is optimal for detection.

Compound class	Ionization mode	Reference
Dioxins	Charge transfer	1
PCBs	Charge transfer	1
Pyrethroids	Protonation	2
Chlorinated pesticides	Charge transfer	3
BDEs	Charge transfer	1
Pesticides	Controlled mixed mode	4

Table 1. Compound classes and preferred ionization mechanism with references.

Once the ionization mechanism has been determined, optimization of key parameters can be performed. Table 2 shows each parameter and the range it should be optimized within. The typical values can be used from the setup section as a starting point. There are three key parameters that will govern sensitivity and ionization efficiency: corona current, cone gas, and auxiliary gas (Table 2). Cone gas is the parameter that

has the largest effect on switching between protonation and charge transfer. The parameters will then be varied one by one to monitor the effect of each. This can be done in an overnight run, changing the parameter in the tune page and saving it in the project. The sample list can then be used to select each tune page in turn. A comparison between the starting conditions can be made using peak area, and the parameters that give the best response can be selected.

Parameter	Charge transfer	Protonation	Controlled mixed mode
Corona current (μA)	1 to 5	2 to 10	2 to 8
Cone gas (L/h)	150 to 250	150 to 200	170 to 220
Auxiliary gas (L/h)	100 to 300	100 to 1000	100 to 500
Make up gas (mL/min)	350	350	350
Cone voltage (V)	30	30	30
Source offset (V)	50	50	50
Source temperature ($^{\circ}\text{C}$)	150	150	150
Modifier	None	Water uncapped	None

Table 2. Tune values and operation range.

Multi-reaction-monitoring (MRMs) can be generated before or after the optimization. This involves using a standard in full scan and selecting an abundant precursor. Product ion scans can then be performed at varying collision energies to determine the MRM transition. This can be done in a single experiment or multiple injections. Multiple compounds can be optimized at the same time. This is advised to be performed in multiple injections to ensure a well-described chromatographic peak. An example of MRM set up for dichloran is shown in Figure 10.

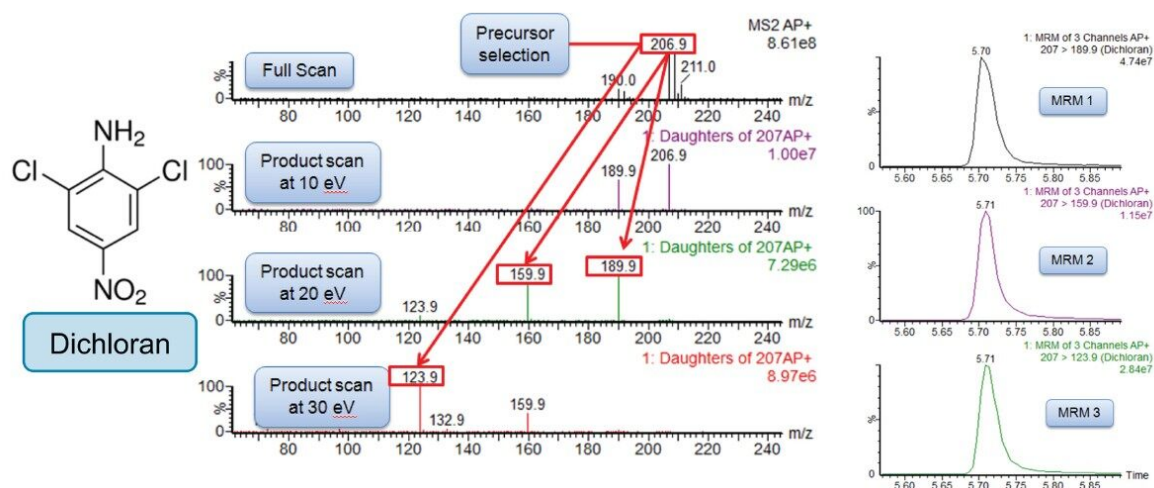


Figure 10. MRM optimization of dichloran.

Maintenance and Troubleshooting

MS maintenance

There is minimal MS maintenance to perform on the APGC. To clean the ionization chamber remove the ceramics and the spring. The ionization chamber should be sonicated for 5 minutes in water, followed by 5 minutes in methanol, and finally 5 minutes in dichloromethane. If there is visible ion burn, aluminum oxide can be used to clean the source followed by the solvent washes. Ensure that the corona pin is sharp by using lapping film.

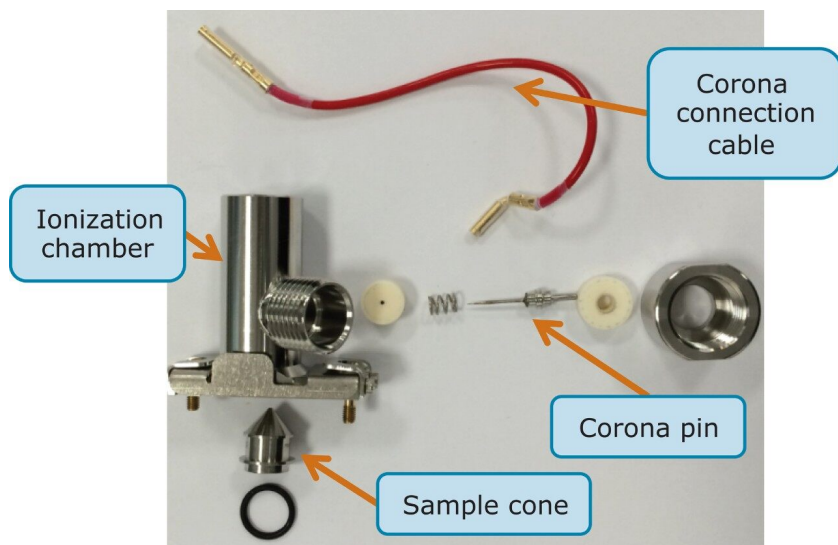


Figure 11. APGC ionization chamber parts.

GC maintenance

When sensitivity is low, or peak shape is poor, GC maintenance should be performed first on the system. The same maintenance as for standard GC is required for APGC. Trimming of the front end of the column and changing of the liner must be performed when required. The inlet, oven, and transfer line should be cooled before turning off the helium gas flow. When installing a new column, or after a liner change or trim, helium should be set to flow for 5 minutes before increasing the temperature. This will prevent any damage to the column.

Ensuring that the column is cut with a straight edge is important as this impacts transfer of the analytes to the head on the column and into the ionization chamber. A ceramic wafer should be used at 45° C to score the column, and the column should be broken away from the cut. The cut can be checked with a magnifying glass. Figure 12 shows a good and bad cut. Setting of the GC column in the injector varies for a split/splitless (SSL) and multimode injector (MMI). It is important to set this correctly, otherwise sensitivity will be detrimentally affected. Figure 13 shows the correct placement.

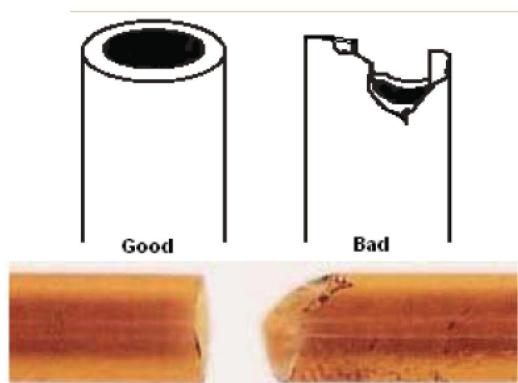


Figure 12. Column cutting.

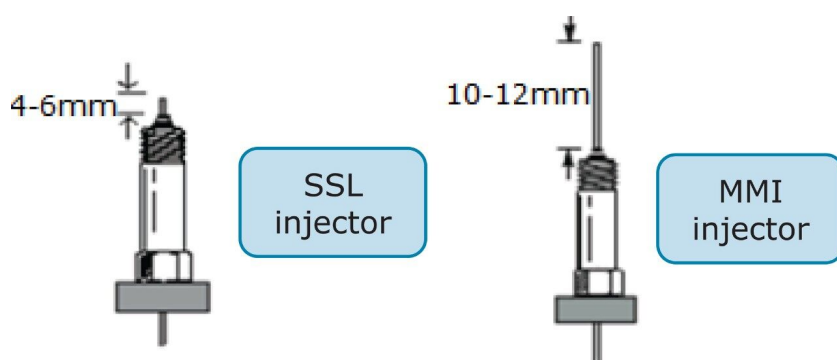


Figure 13. Setting of the column in the injector.

Compounds with high boiling points

There are two ways to avoid peak tailing for high temperature boiling compounds. First, try increasing the transfer line temperature to aid the transit of high boiling compounds into the ionization chamber. If this is not permitted by the column's maximum operating temperature, deactivated fused silica could be fitted in the heated transfer line. By adding a retention gap the potential activity towards high boiling compounds is reduced. It is recommended to use the Siltek Guard column from RESTEK, (P/N 100026). The maximum temperature of this retention gap is 380 °C which should be sufficient for most applications. The SilTite Union to make the connection can be purchased from SGE, (P/N 073560).

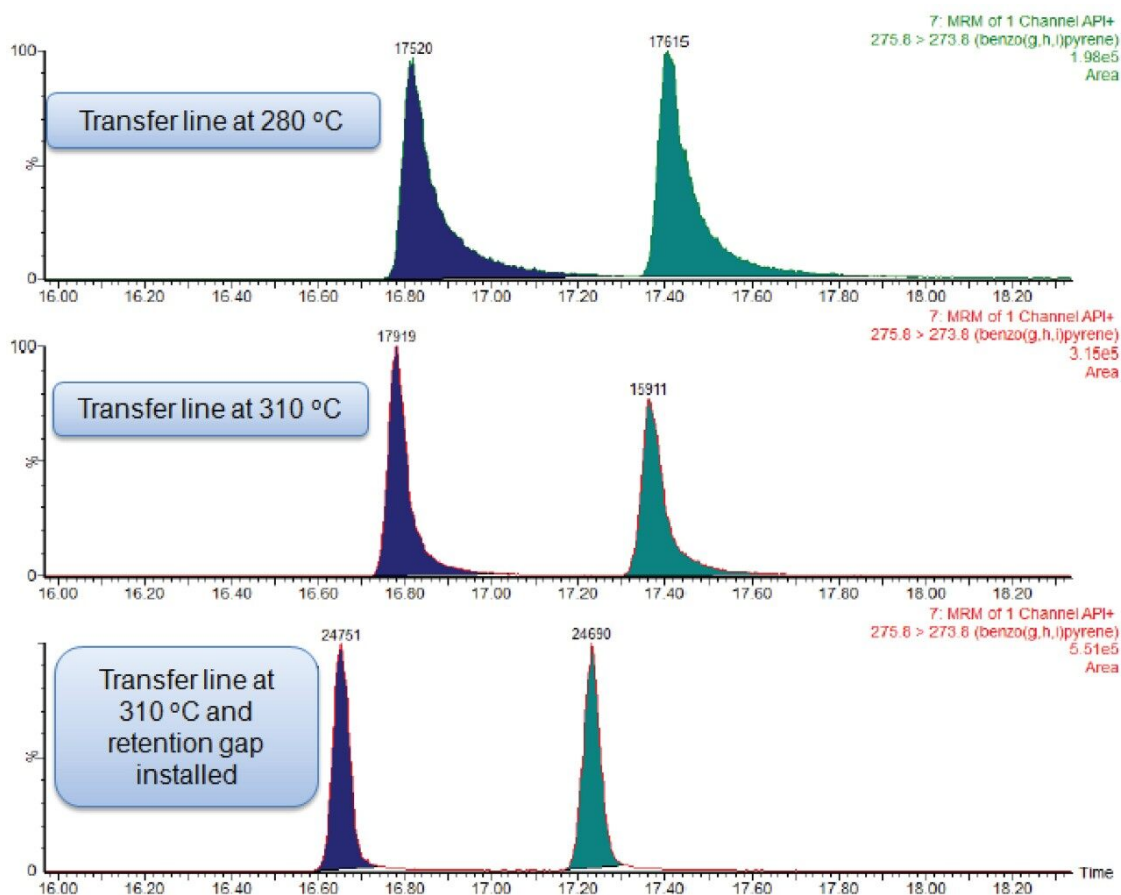


Figure 14. Tailing reduction of PAHs benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene by increasing the temperature of the transfer line and fitting a retention gap.



Figure 15 SilTite μ -Union connect column and retention gap.

References

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