

Increasing Throughput in GC Environmental Methods

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Overview

This poster describes methods for increasing the throughput of environmental samples using a typical sample. A mixture of polynuclear aromatic hydrocarbons (PAHs) is used to demonstrate the effects of varying GC conditions and parameters with the aim of reducing run times.

Introduction

The pressure of heavy workload and the continuing need to improve productivity in a modern environmental laboratory requires a high throughput of samples. With advances in sample preparation methods, GC analysis time is becoming the rate determining step for many analyses.

This poster discusses alternative methods for speeding up environmental analyses using both conventional and UltraFast GC using a range of TRACE™ TR-SMS 5% phenyl polysilphenylene-siloxane coated columns.

Key to the discussion is the reduction in analysis time using readily available techniques such as alteration of column length, oven temperature ramp, column ID and film thickness. UltraFast GC is also demonstrated.

The sample used for the comparison is the 15 component standard mixture used in EPA 610, analysis of polynuclear aromatic hydrocarbons. The EPA method is antiquated and describes a 45 minute analysis using a packed column containing OV™-17 as follows:

Method EPA 610

Column Type: 1.8 m x 2 mm ID glass column packed with Chromosorb™ W-AW-DCMS coated with 3% OV-17

Run Conditions
Carrier Gas: Nitrogen
Gas Flow Rate: 40 mL/min
Initial Temp: 100 °C for 4 min
Ramp 1: 8 °C/min up to 280 °C and hold

Detector Type: FID

Method Limitations
Four pairs of peaks remain unresolved using this technique (pairs marked *)

Total run time is 45 minutes

Table 1. Compounds in Standard EPA 610 on packed Column

Compound	Retention Time
1) Naphthalene	4.2
2) Acenaphthylene	10.2
3) Acenaphthene	10.8
4) Fluorene	12.6
5) Phenanthrene	15.9*
6) Anthracene	15.9*
7) Fluoranthene	19.8
8) Pyrene	20.6
9) Benzo[a]anthracene	24.7*
10) Chrysene	24.7*
11) Benzo[b]fluoranthene	29.0*
12) Benzo[k]fluoranthene	29.0*
13) Benzo[a]pyrene	29.4
14) Dibenz[a,h]anthracene	36.2*
15) Indeno[1,2,3-cd]perylene	36.2*
16) Benzo[ghi]perylene	36.6

Advantages of Using Capillary GC

A 5% phenyl capillary column elutes the analytes in the same order as the OV-17 packed column with the advantages of improved resolution, speed and sensitivity.

Initial capillary GC methods attempted to simulate the packed column method with a run time of 45 minutes. The example below shows a method where the oven programme was slowed down to keep the run time similar to the packed column method; helium has been substituted for the original nitrogen carrier gas.

However with the increasing pressures on analysis time, and the flexibility within the EPA 610 method, it has been possible to greatly reduce run time by altering sign GC variables.

Variables Affecting Run Time

A number of variables within the GC setup can be manipulated to alter the run time, bearing in mind the need to maintain resolution, elution order and sensitivity.

Table 2. Variables Affecting GC Run Time

Temperature ramp rate	Higher starting temperature and a steeper heating rate make peaks elute faster.
Column length	Shorter column = faster run time
Carrier gas flow rate or control mechanism	Each gas type has an optimum linear flow range within which speed can be adjusted.
Film thickness	Thicker film = more interaction of solutes = slower elution
Column internal diameter (ID)	Reducing ID increases column efficiency.
Ultra Fast technology	Combination of short column, small ID, thin film, special ultra fast heating coil (2 °C/sec) and fast FID detection.

Methodology

All columns are 5% phenyl polysilphenylene-siloxane coated TRACE TR-SMS columns (Thermo Electron Corporation, Bellefonte, PA). Dimensions are as specified against each example.

Columns A, B, C and D were mounted in a TRACE GC Ultra™ with a TriPlus™ autosampler (Thermo Electron Corporation, Milan, Italy) fitted with a FID detector. Helium was used as the carrier gas and flow rates and oven programs were optimized to the column dimensions as detailed in each example. The system was run in either constant flow or constant pressure mode as indicated.

Column E uses UltraFast GC technology fitted to a TRACE GC Ultra (Thermo Electron Corporation, Milan, Italy). The carrier gas used was hydrogen. UltraFast GC provides improvements in analysis time of between 10 and 20 fold over traditional GC. This is achieved via a combination of high speed column heating (2 °C/second) and fast FID detection. This work was carried out by Paolo Magni of Thermo Electron Corporation, Milan.

Results and Discussion

Figure 1. Column A - Simulation of Packed Column Analysis

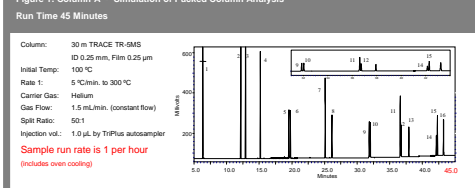


Figure 1: Simulation of packed column analysis performed on a 30 m capillary column. Carrier gas was changed from nitrogen to helium and compared with the 3% OV-17 packed column, the 5% phenyl polysilphenylene capillary column separates all 4 of the unresolved peak pairs in a similar run time (see inset). The first strategy for reducing run time should be to modify the oven ramp increasing heating where the peaks are well separated and introducing a slow ramp where extra separation is required as in Figure 2.

Figure 2. Column A - Effect of Increasing Temperature Ramp

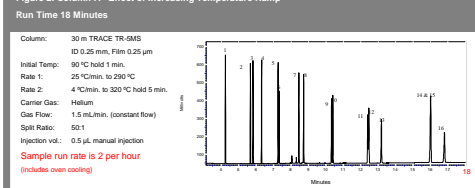


Figure 2: Optimization of the oven program has cut the run time by more than half without changing any other parameters. There is some loss of resolution between peaks 14 and 15 compared with the 45 minute run; however, the extra specificity of a MS detector would resolve these peaks. Reducing column length is a second strategy for reducing run time. (Figure 3, 15 m column). Note the need to increase the oven ramp rate in order to elute the high boiling materials whilst retaining peak shape.

Figure 3. Column B - Effect of Reducing Column Length from 30 m to 15 m
Run Time 10 Minutes

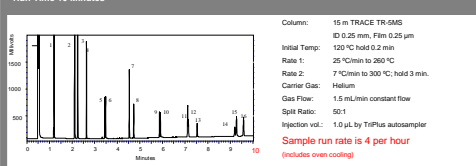


Figure 3: Illustration of effect of simply reducing column length by half and using constant flow. By using a constant pressure setting of 137 kPa, the sample can be run in a shorter time of 7.5 minutes, allowing 5 samples per hour to be run. Contact us for further details on running at constant pressure.

Figure 4. Column C - Effect of Increased ID
Run Time 9 Minutes

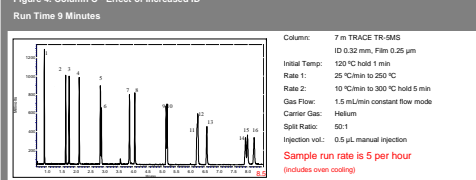


Figure 4: The 7 m column illustrates the effect of film thickness on run time. Although the 7 m column is shorter than the 15 m used in Figure 3, the larger ID makes the column less efficient. Therefore, to maintain the resolution a similar oven programme is needed, making the analysis time only slightly shorter than the 15 m.

Figure 5. Column D - Effect of Reducing Column ID and Film Thickness
Run Time 5 Minutes

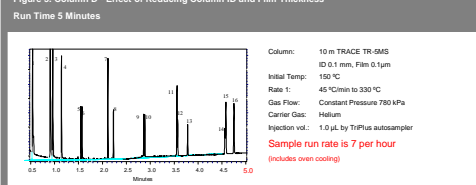


Figure 5: The combination of using a narrower 0.1 mm column coated with a thinner film is another strategy for faster analysis. In comparison with the 7m 0.25um film column, the longer 10m x 0.1um film is faster. In addition, using constant pressure has enhanced the analysis speed down to under 5 minutes. The effect of running at constant pressure is to greatly speed up the linear velocity at the beginning of the run where the peaks are well separated. Later in the run, when the temperature is high, the velocity is lower allowing more dwell time on the column for the later peaks which elute close together.

Figure 6. Column E - Effect of UltraFast Technology
Run Time 2.5 Minutes

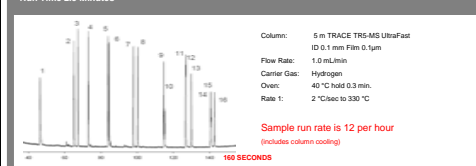


Figure 6: The UltraFast column and detector can run sample in just 160 seconds improving sample throughput to approx 12 per hour. At this point, the limiting factor becomes the ability of the column to cool quickly enough between runs and the sampling rate of the detector. In addition to a fast heating coil to facilitate ramping, a fast FID detector or Time of Flight (TOF) MS is required to achieve the sampling rate across individual peaks.

Conclusions

In this poster we have demonstrated a number of simple methods of accelerating sample analysis which could greatly improve the productivity of environmental testing laboratories.

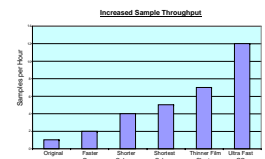


Table 3. Increasing Throughput of Environmental Sample EPA610

METHOD	RUN TIME	RUNS PER HOUR
Original EPA 610 - Table 1 and Figure 1	45 minutes	1
Increase Oven Temperature Ramp Rate - Figure 2	18 minutes	2
Reduce Column Length - Figure 3	10 minutes	4
Reduction in run time from 18 minutes to 9 minutes is due to shorter column length		
Increase in Column ID - Figure 4	9 minutes	5
Thicker film = more interaction between mobile and stationary phase = slower elution somewhat offsetting the advantage of shorter length		
Reduction in Column ID and Film Thickness - Figure 5	5.0 minutes	7
Reduction in run time to under 5 minutes using constant pressure.		
Use of UltraFast Technology - Figure 6	2.5 minutes	12
Combination of short column, fast heating, narrow ID, thin film, H ₂ carrier gas and fast detector gives run time under 2.5 minutes.		

References:

EPA Method 610 www.epa.gov/epahome/index/

Additional Information:

For further information please go to www.thermo.com/columns

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