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Fast GC-MS/MS Analysis of Polyaromatic Hydrocarbons using Waters Quattro micro GC

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Abstract

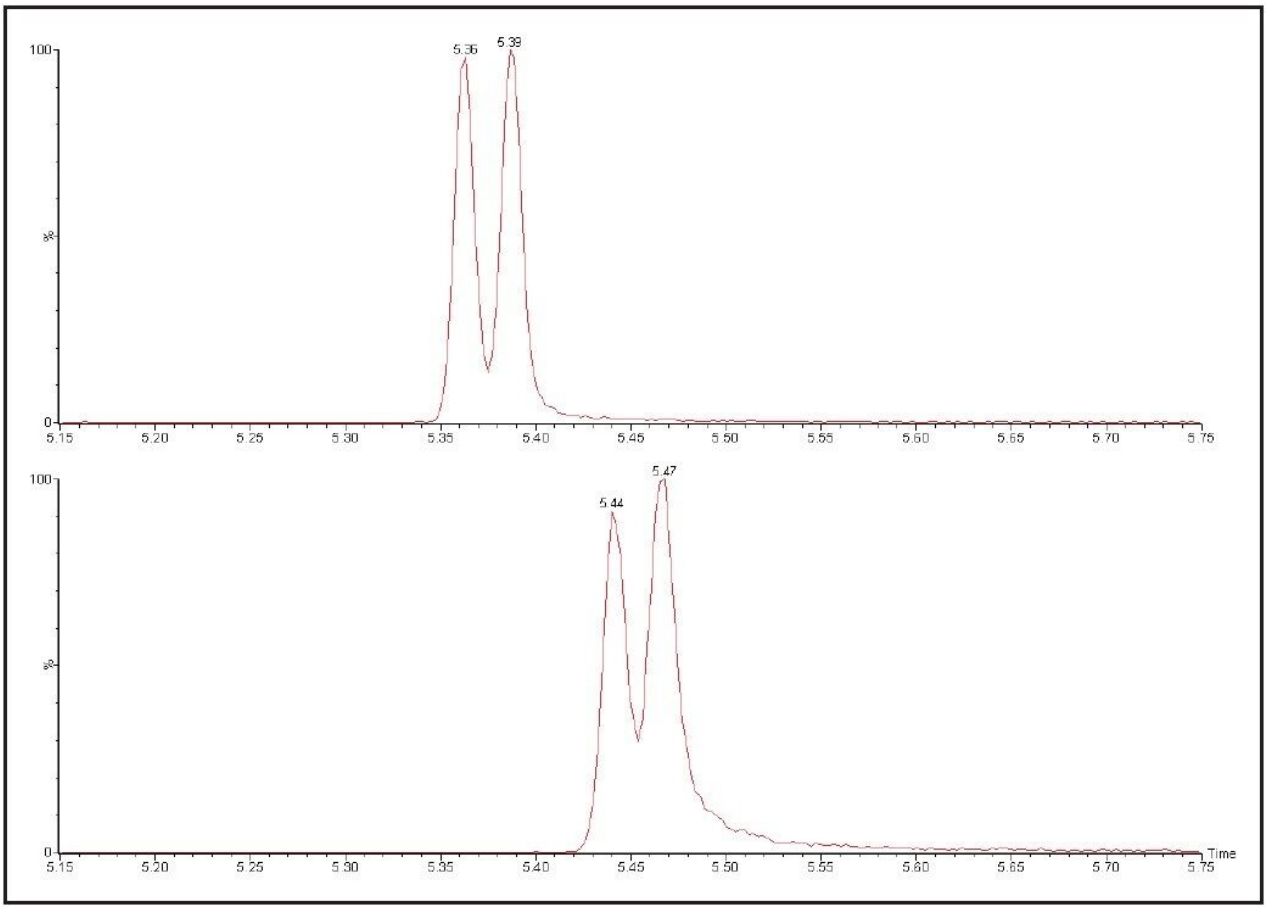
This application note demonstrates fast GC-MS/MS analysis of polyaromatic hydrocarbons using Waters Quattro micro GC.

Introduction

Fast GC

GC-MS analysis of polyaromatic hydrocarbons (PAHs) is recognized as one of the most sensitive methods for the analysis of these persistent organic pollutants (POPs). PAHs are easily resolved using standard GC columns without a requirement for derivatization. Most separations can be achieved in less than 30 minutes using columns such as 30 m 0.25 mm ID 0.25 µm df 5% phenyl polysiloxane type phases. The use of a narrow bore, thin film column allows an increase in chromatographic resolving power, coupled with a reduction in analysis time.

As the column ID is reduced, the column efficiency increases. For example, a column of 0.25 mm ID has 2,500 plates per meter, whereas a column of 0.1 mm ID has 6,700 plates per meter. The injection volume is critical to avoid overloading of the GC Column. Figure 1 shows that injecting half the volume of a standard onto the column can give greater intensity and better chromatography. The figure shows benz(a)anthracene and chrysene acquired under fast GC conditions, using 0.5 µL and 1 µL injection volume onto a 0.18 mm ID GC Column.



Experimental

Fast GC-MS/MS

The column used for this analysis was a DB5-ms 20 m 0.18 mm ID 0.18 µm df Column with a constant He flow rate of 0.7 ml min^{-1}, installed in an Agilent 6890 GC oven, directly interfaced to a Waters Quattro micro GC Mass Spectrometer operated in EI+ mode. The GC oven was fitted with a fast GC oven insert, and was configured in the fast oven ramping mode. All injections were made in pulsed splitless mode with an injection volume of 0.5 µL, using a purge time of 0.4 minute, 0.4 min pulse (280 kPa). The GC temperature ramp employed was: - 50 °C/0.4 min, 100 °C min^{-1} to 90 °C, 65 °C min^{-1} to 190 °C, 50 °C min^{-1} to 265 °C, 40 °C min^{-1} to 310 °C, hold 4 minutes. The GC ramp and column combination employed results in peak widths of between 0.9 and 3 seconds, with a run time of less than 9 minutes. All critical pairs were suitably resolved under these conditions. Figure 2 shows the separation for phenanthrene and anthracene (top trace) and

benzo(b)fluoranthene, benzo(k)fluoranthene and benzo[a]pyrene (bottom trace).

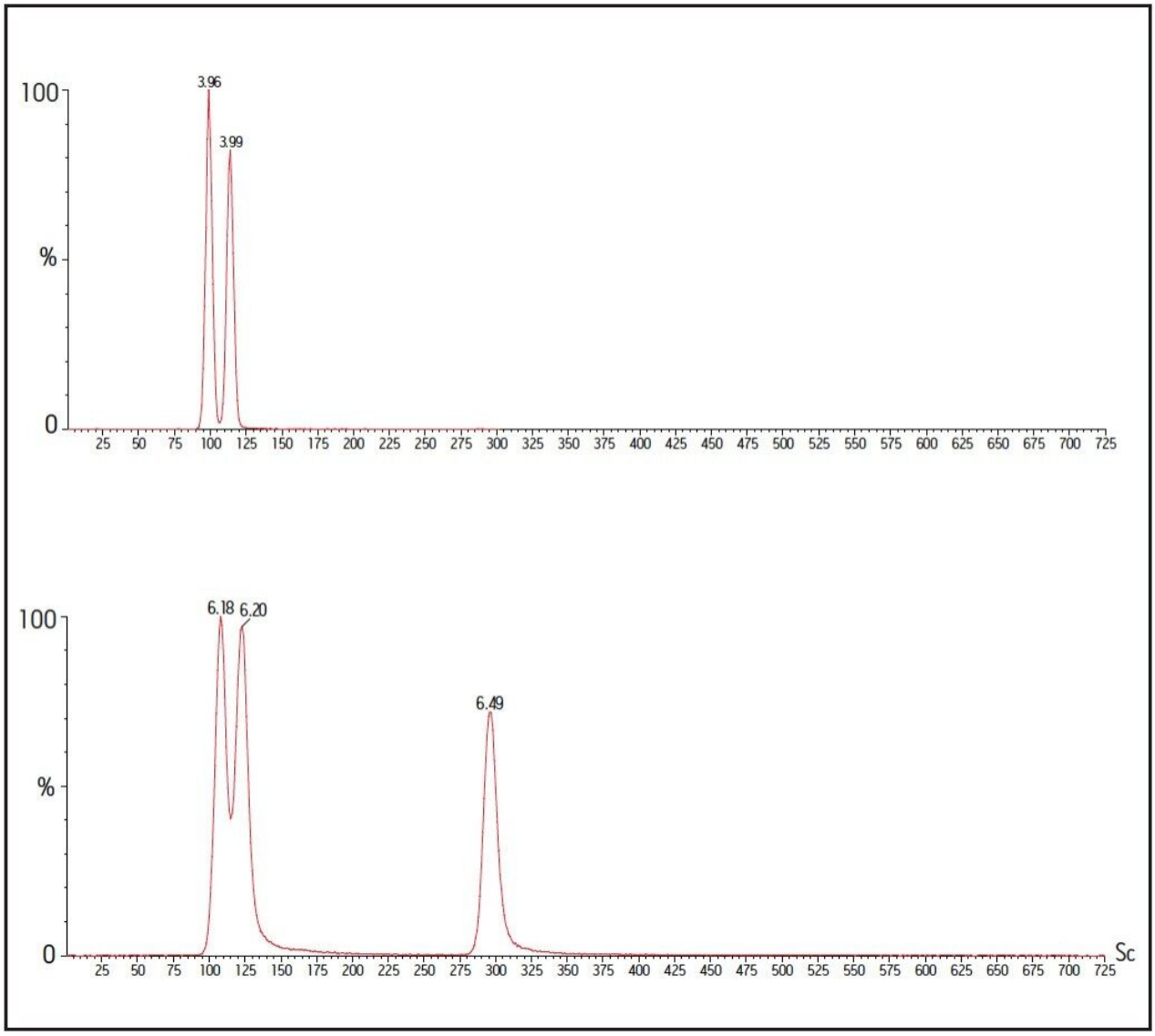


Figure 1. Separation and intensity for 0.5 µL injection (top trace) and 1 µL injection (bottom trace) for benz(a)anthracene and chrysene under fast GC conditions.

Results and Discussion

Figure 2 also shows the number of scans across each peak with a minimum of 8 data points per peak. This is possible due to the ability of the Quattro micro GC to acquire with dwell times and interchannel delay times

of 10 ms. The top chromatogram shows 12 data points across a GC peak 1.2 seconds wide; while acquiring 3 MRM channels simultaneously. This exceeds the quantitative requirement for a minimum of 8 data points.

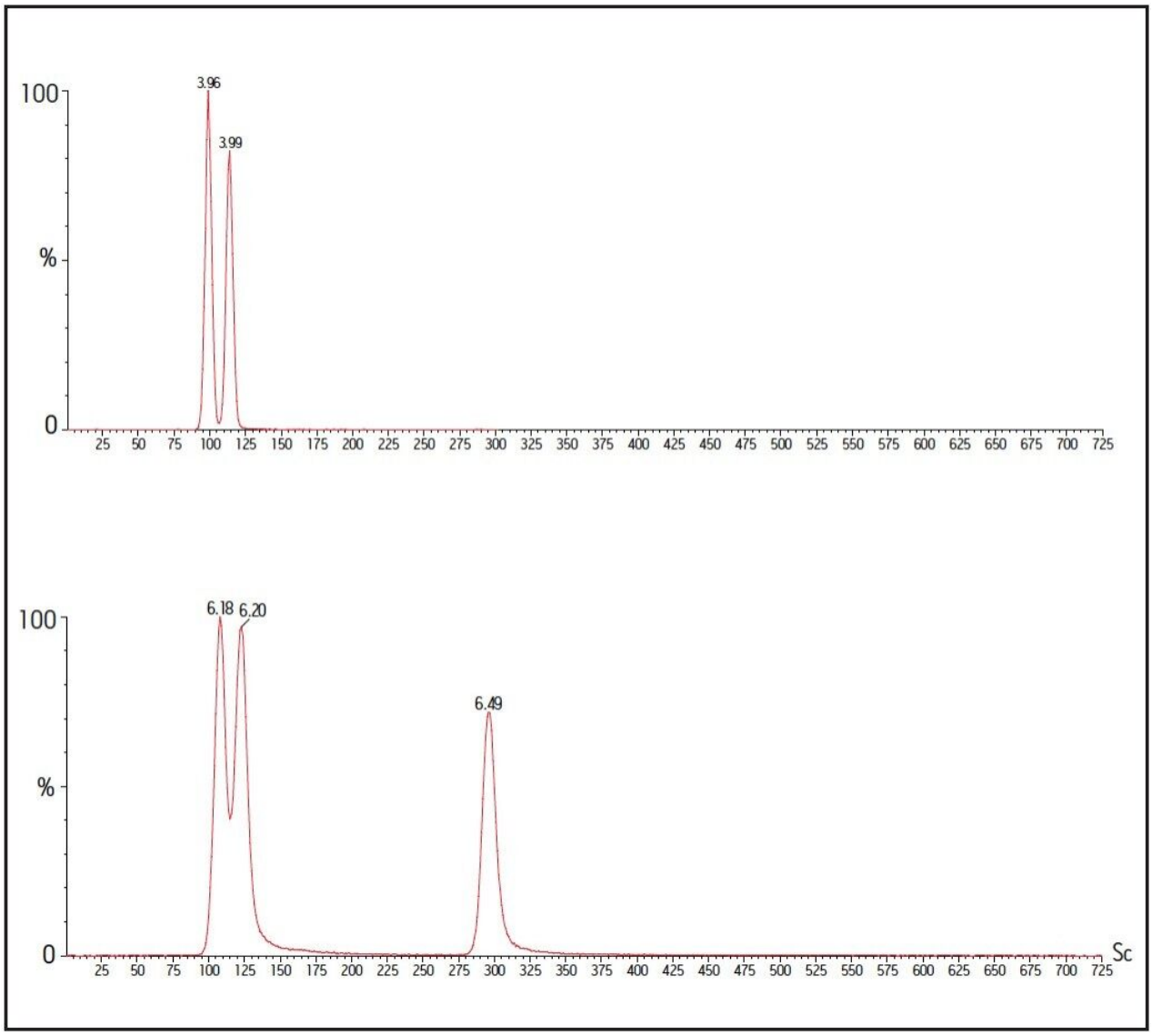


Figure 2. Critical pairs separation showing number of data points (scans) across each peak.

All US EPA 16 PAHs were separated and determined with the last eluting peak eluting at 8.21 minutes. Excellent linearity was observed over a concentration range from 0.25 pg to 250 pg on column, with all LODs (based upon peak to peak signal to noise of 3:1) being 0.25 pg or less. Table 1 presents the r^2 values, retention times and LODs for the US EPA 16 PAHs. The linear dynamic range is affected when acquiring fast GC because the loading capacity of the column is exceeded at lower concentrations due to the narrow peak widths. Comparing the LODs determined with those acquired under 'normal' chromatographic conditions,

fast GC operation can be seen to give a significant sensitivity improvement. The calibration curves acquired were linear up to 250 pg, but above this concentration, the dynamic range of the column is exceeded when acquiring under these conditions.

Name	RT	Coeff. of Determination	LOD (pg)	MRM1	eV	MRM2	eV	MRM3	eV
Naphthalene	2.59	0.999	0.1	128>128	15	128>102	20	128>78	20
Acenaphthene	3.22	0.996	0.2	152>151	20	152>150	25	n/a	n/a
Acenaphthylene	3.29	0.997	0.1	154>153	20	154>152	30	n/a	n/a
Fluorene	3.52	0.100	0.1	166>165	20	166>164	35	n/a	n/a
Phenanthrene	3.97	0.999	0.12	178>151	40	178>152	15	n/a	n/a
d10-Anthracene	3.98	n/a	n/a	188>160	20	n/a	n/a	n/a	n/a
Anthracene	3.99	0.999	0.17	178>151	40	178>152	15	n/a	n/a
Fluoranthene	4.56	0.998	0.1	202>202	20	202>200	35	202>150	45
Pyrene	4.68	0.999	0.1	202>202	20	202>200	35	202>150	45
Benz(a)anthracene	5.36	0.999	0.1	228>226	30	228>228	25	228>202	30
Chrysene	5.39	0.999	0.1	228>226	30	228>228	25	228>202	30
Benzo[b]fluoranthene	6.18	0.999	0.12	252>250	30	252>252	25	252>224	47
Benzo[k]fluoranthene	6.21	0.999	0.2	252>250	30	252>252	25	252>224	47
Benzo[a]pyrene	6.49	0.998	0.2	252>250	30	252>252	25	252>224	47
Indeno(1,2,3-cd)pyrene	7.84	0.997	0.25	276>274	40	276>276	25	276>248	50
Dibenz(a,h)anthracene	7.87	0.996	0.2	278>276	35	278>278	25	278>274	55
Benzo[ghi]perylene	8.21	0.997	0.2	276>274	40	276>276	25	276>248	50

Table 1. Retention time, coefficient of determination, LOD and MRM transitions for each of the PAHs analyzed.

The MRM transitions optimized for the PAHs are given in Table 1. All transitions were optimized with a collision cell gas pressure of $3e^{-3}$ mbar (Argon). In some cases, parent to parent MRM transitions are quoted. In these cases, a third transition has been optimized, because parent to parent transitions may not always offer adequate selectivity in the presence of a matrix, especially the hydrocarbon matrix often encountered during PAH analysis.

The comparative sensitivity for injections of a spiked 0.1 μgL^{-1} canal water extract is shown in Figures 3 and 4. Figure 3 shows a 1 µL injection of the sample extract acquired under standard chromatographic conditions. Figure 4 shows a 0.5 µL injection of the same extract acquired using the fast GC conditions described above. It can be seen that the sensitivity has more than doubled, while maintaining good chromatographic resolution.

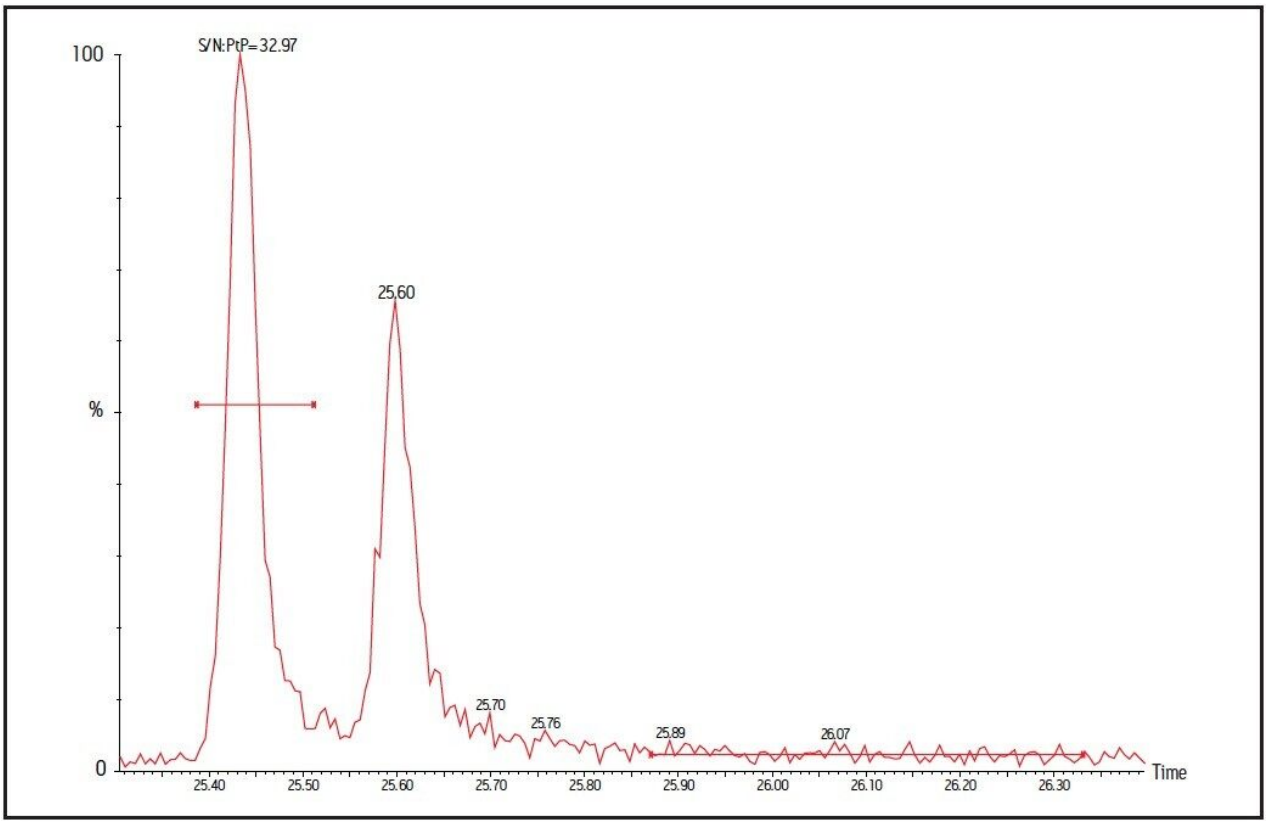


Figure 3. 1 µL injection of 0.1 µgL^{-1} canal water extract acquired using standard chromatographic conditions.

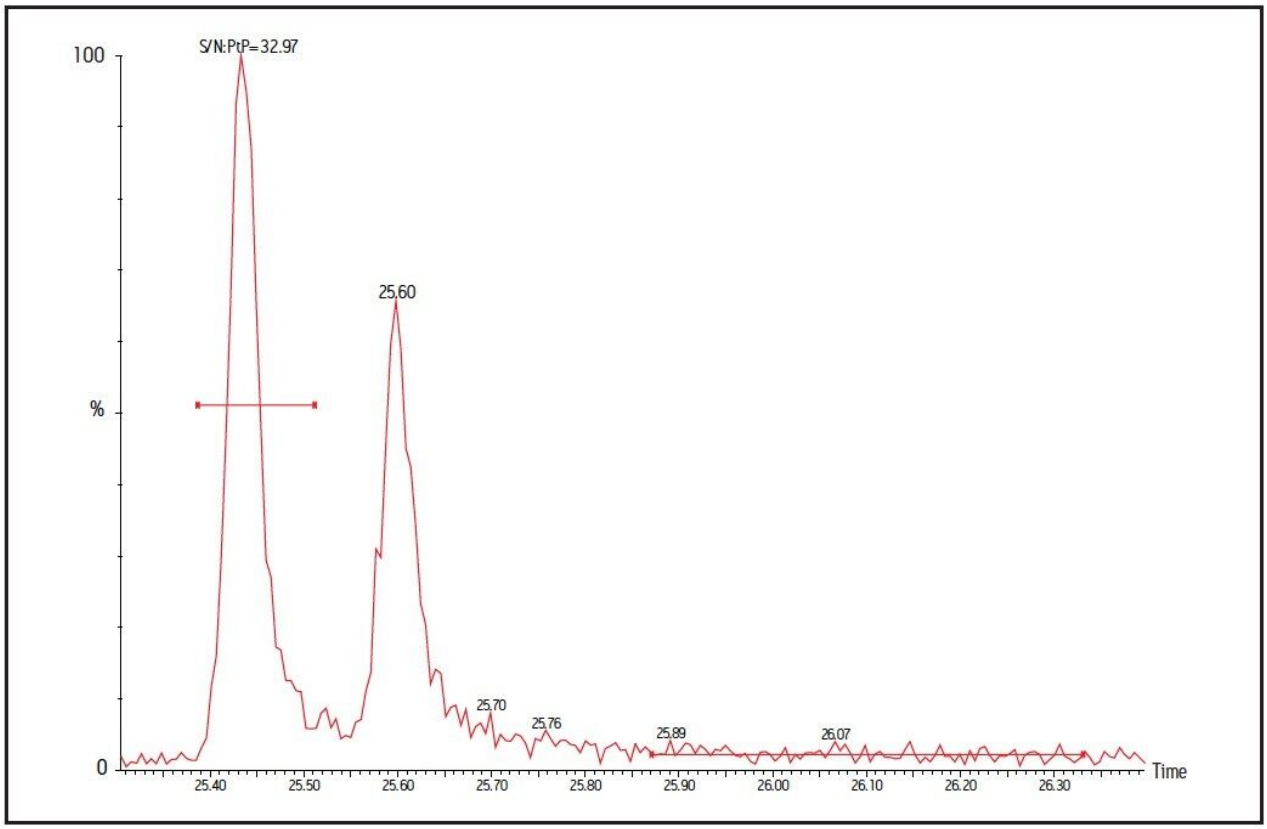


Figure 4. 0.5 µL injection of 0.1 µgL^{-1} canal water extract acquired using fast GC conditions.

Conclusion

This example of polyaromatic hydrocarbon analysis using fast GC chromatographic conditions clearly demonstrates the ability of the Quattro micro GC to acquire data using very short dwell times. All data was acquired using 10 ms dwell and inter-channel delay times when using fast chromatographic conditions, with the exception of the last eluting peaks, where longer dwell times could be utilized due to the broader chromatographic peaks. This is enabled by the ability of Waters MassLynx Software control to allow flexible dwell times within an acquisition function. This allows the user to maximize the time spent monitoring transitions when necessary. Fast GC conditions can be used to enhance the sensitivity of a method. However, this enhancement comes at the cost of reduced dynamic range due to column loading capacities.

The data presented here shows that it is possible to determine all US EPA 16 PAHs within a 9-minute analytical run time, without compromising chromatographic resolution.

720001910, June 2007