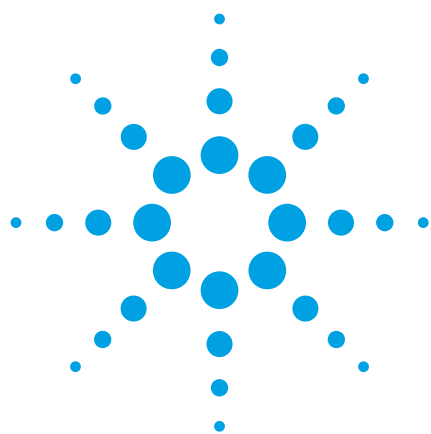




Complex polycyclic aromatic hydrocarbons from coal tar on Agilent J&W Select PAH

Application Note

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Introduction

Coal tar is a brown or black liquid of high viscosity, which smells of naphthalene and aromatic hydrocarbons and is obtained from the destructive distillation of coal. Formerly, coal tar was obtained as a by-product in manufacturing coal gas. It is now produced in making coke for steel making. The crude tar contains a large number of organic compounds, such as benzene, naphthalene, methylbenzene and phenols, which can be obtained by distillation. The residue is pitch. At one time coal tar was the major source of organic chemicals, most of which are now derived from petroleum and natural gas. Coal tar pitch is mainly used as a binding agent in the production of carbon electrodes, anodes and Søderberg electrodes, for example, by the aluminium industry. It is also used as a binding agent for refractories, clay pigeons, active carbon, coal briquetting, road construction and roofing. Furthermore, small quantities are used for heavy-duty corrosion protection.

The standard coal tar reference material (SRM 1597a, NIST) is a natural, combustion-related mixture of polycyclic aromatic hydrocarbons (PAHs), isolated from a medium crude coke-oven tar and dissolved in toluene. However, PAHs can be difficult to analyze because some of them have the same mass. This makes their separation with GC/MS problematic, and so column selectivity and an optimized oven program are necessary to resolve these PAHs. In this application note, a coal tar sample was analyzed using an optimized oven program for the Select PAH column. As the coal tar sample is intended for use in the evaluation and validation of analytical methods for the determination of PAHs, we can clearly show the performance of the Select PAH with this reference material.



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Conditions

Technique:	GC/MS, Triple Quad
Column:	Select PAH, 30 x 0.25 mm, df=0.15 μ m (part number CP7462)
Sample:	SRM 1597a, concentration approximately 0.8-21 μ g/mL (www.nist.gov)
Injection Volume:	0.1 μ L
Temperature:	70 °C (0.70 min), 85 °C/min, 180 °C, 3 °C/min, 230 °C (7 min), 28 °C/min, 280 °C (10 min), 14 °C/min, 350 °C (3 min)
Carrier Gas:	Helium, constant flow 2.0 mL/min
Injector:	300 °C, Splitless mode, 1 min @ 50 mL/min
Detector:	Triple Quad, EI in FS or SIM mode, ion source 275 °C, transfer line 300 °C

space and the large number of possible configurations of the PAHs. The relatively long run time of 45 min at the maximum programmable temperature of 350 °C may affect the column lifetime.

Results and Discussion

The sample was analyzed directly in full scan and SIM mode. PAHs were analyzed using the same conditions as for a standard with regulated and interfering PAHs, which made their identification possible. Chromatograms with identifications are shown in Figures 1 to 3. It can be seen from Figure 1 that chrysene (66 mg/kg) was separated from triphenylene (12 mg/kg), and benzo[b,k,j]fluoranthene (66, 37 and 41 mg/kg) from benzo[a]pyrene (94 mg/kg). The MS spectrum from chrysene is shown. As well as the molecular ion (M^+) m/z 228, other ions such as m/z 226 and m/z 229 were formed. The PAHs were mostly very stable and only low fragment ions were observed, such as m/z 113 and 114 in this mass spectrum.

In addition, a group-type analysis of high molecular weight PAHs was possible, which is shown in Figure 4. PAHs with higher molecular weight ($MW > 302$) were eluted at 350 °C due to the maximum programmable column temperature. Many isomers of high molecular weight were in the coal tar sample. Complete separation, however, was not possible on a single column because of the limited separation

Table 1. Peak Indication for Figure 1

BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BpFA	Benzo[b]fluoranthene
BkFA	Benzo[k]fluoranthene
BjFA	Benzo[j]fluoranthene
CHR	Chrysene
CPP	Cyclopenta[c,d]pyrene
TP	Triphenylene

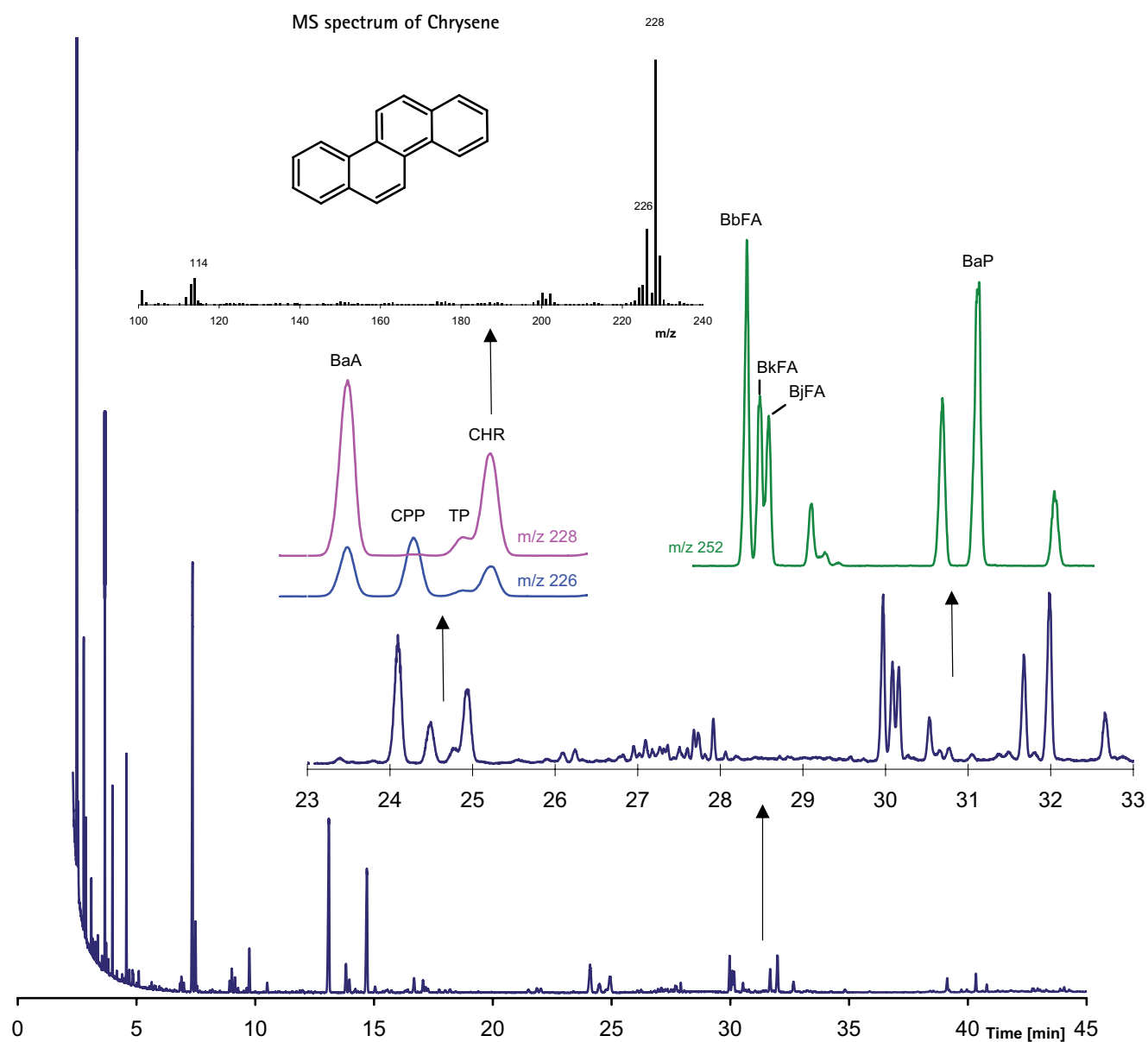


Figure 1. GC/MS analysis of SRM 1597a (0.1 μ L) in full scan mode on Select PAH

Table 2. Peak Indication for Figure 2

ACL	Acenaphthylene (263 mg/kg)
BaA	Benzo[a]anthracene (98 mg/kg)
BaP	Benzo[a]pyrene (94 mg/kg)

BghiP	Benzo[g,h,i]perylene (51 mg/kg)
DBaP	Dibenzo[a,e]pyrene (9 mg/kg)
FA	Fluoranthene (327 mg/kg)

NA	Naphthalene (1030 mg/kg)
PHE	Phenanthrene (454 mg/kg)
PY	Pyrene (240 mg/kg)

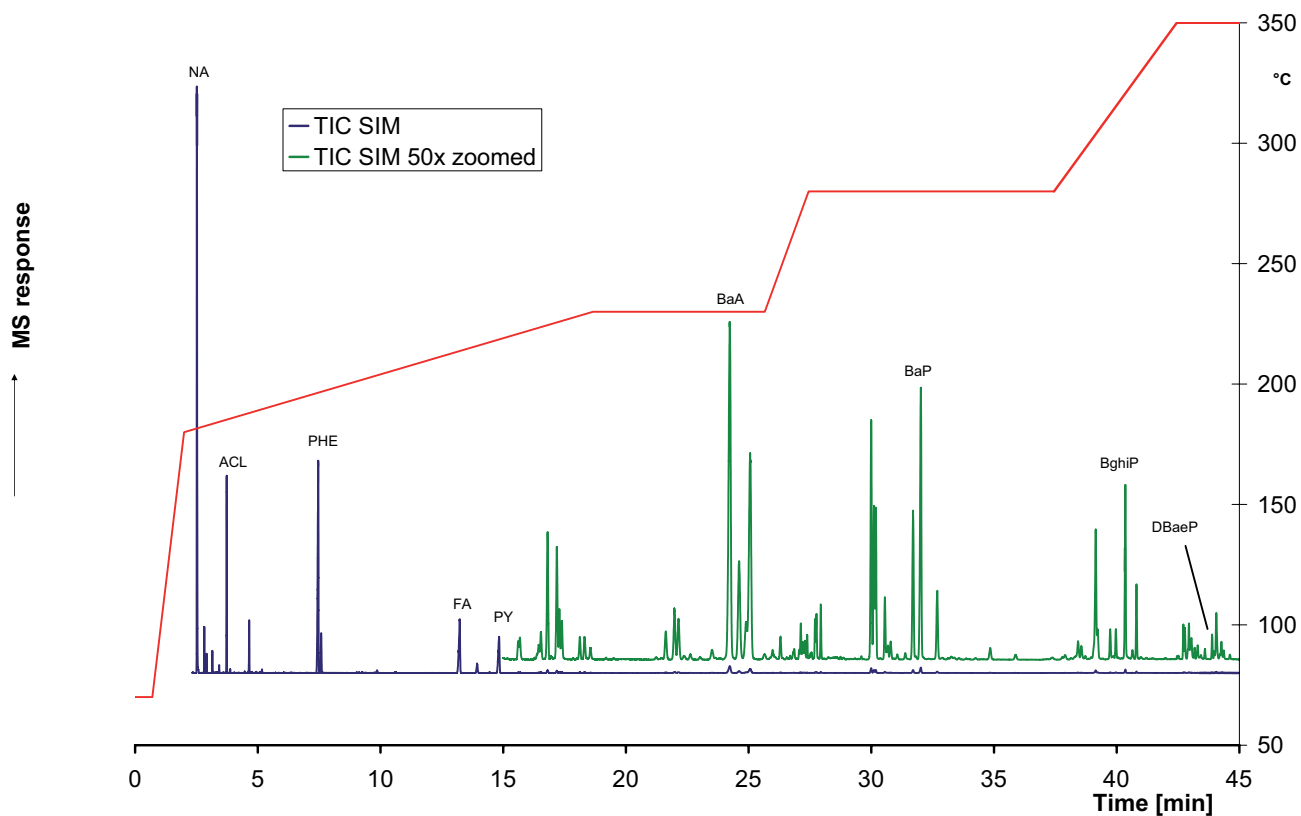


Figure 2. GC/MS analysis of SRM 1597a (0.1 µL) in SIM mode on Select PAH. The final part of the chromatogram is enlarged because of the large concentration difference in the sample

Table 3. Peak Identification for Figure 3

ATR	Anthanthrene (Dibenzo[def,mno]chrysene)
BaFA	Benzo[a]fluoranthene
BaFL	Benzo(a)fluorene
BaP	Benzo[a]pyrene
BbCHR	Benzo[b]chrysene
BbFA	Benzo[b]fluoranthene
BbFL	Benzo(b)fluorene
BbNTP	Benzo(b)naptho(2,1-d)thiophene

BbPer	Benzo[b]perylene
BbTP	Benzo[b]triphenylene
BcFL	7H-benzo[c]fluorene
BeP	Benzo[e]pyrene
BghiP	Benzo[g,h,i]perylene
BjFA	Benzo[j]fluoranthene
BkFA	Benzo[k]fluoranthene
Cor	Coronene
DBaA	Dibenzo[a,h]anthracene

DBaP	Dibenzo[a,e]pyrene
DBaP	Dibenzo[a,h]pyrene
DbaiP	Dibenzo[a,i]pyrene
DBaP	Dibenzo[a,l]pyrene
IP	Indeno[1,2,3-c,d]pyrene
6MC	6-Methylchrysene
5MC	5-Methylchrysene
Per	Perylene
Pic	Picene

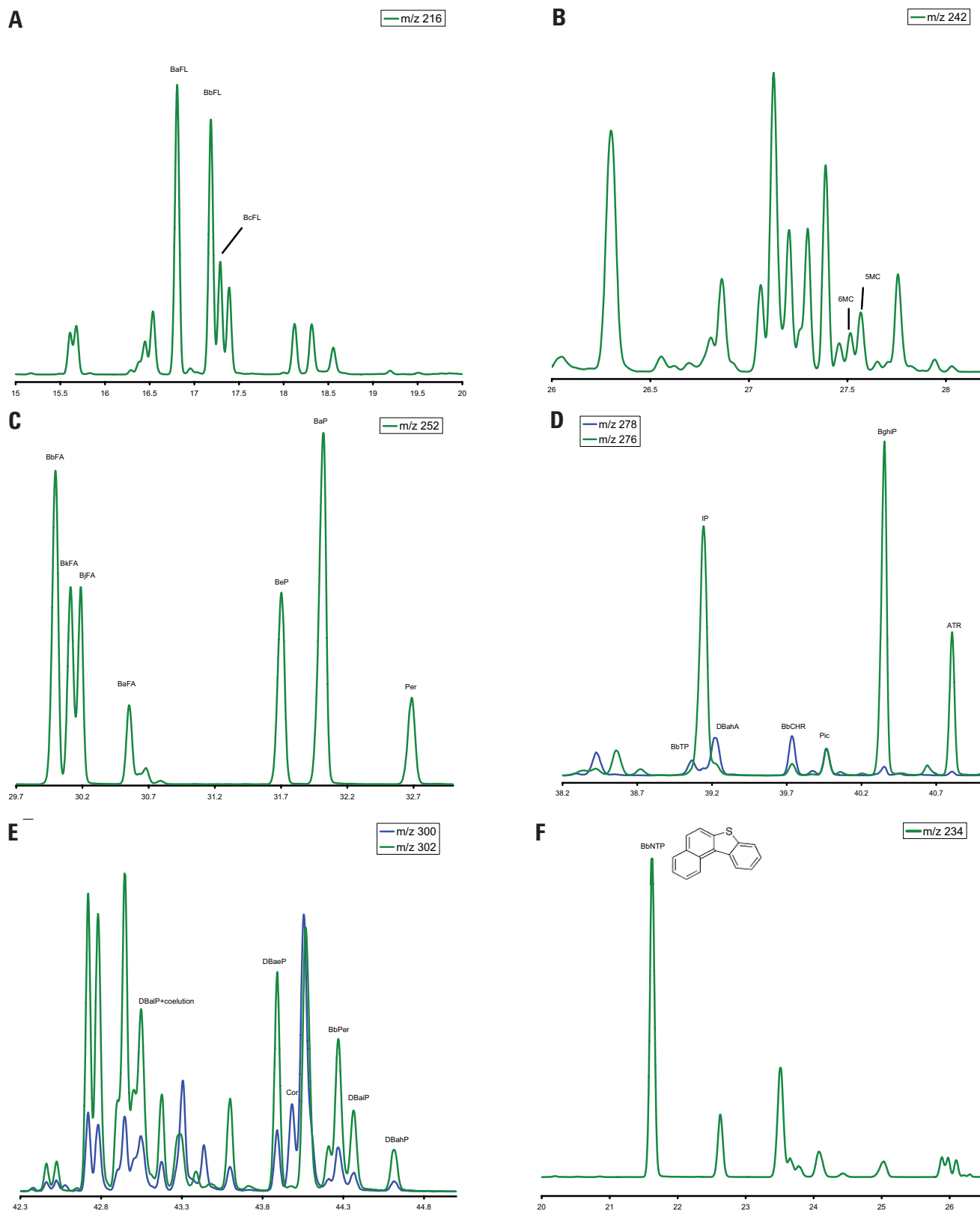


Figure 3. GC/MS analysis of SRM 1597a (0.1 μ L) in SIM mode on Select PAH. Some examples of critical separations are shown: A. Benzofluorenes, B. Methylchrysenes, C. Benzofluoranthenes and isomers, D. Dibenzoanthracenes and isomers, E. Dibenzopyrenes and isomers, F. Benzo[b]naphtho[] thiophene isomers

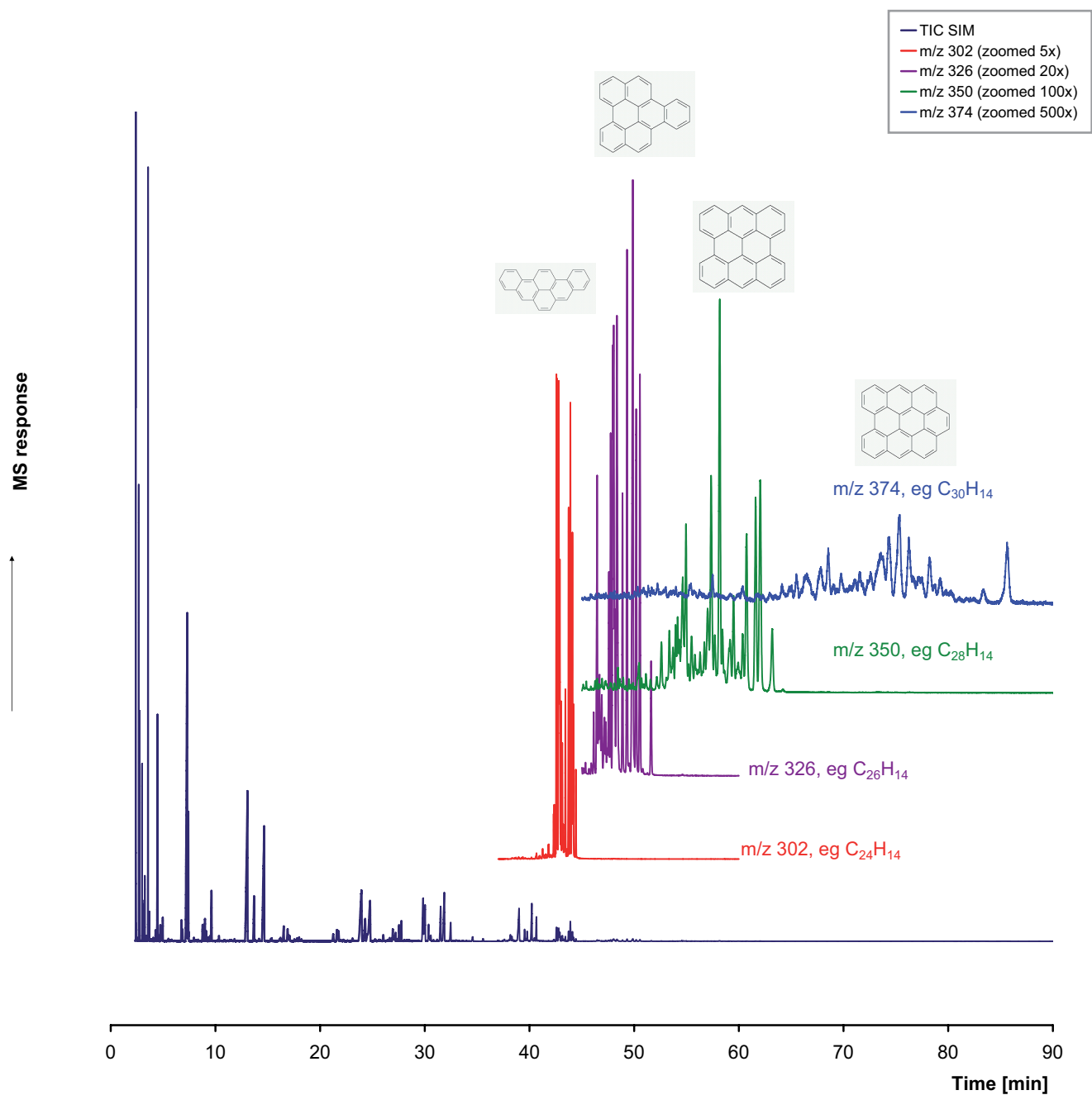


Figure 4. GC/MS analysis of SRM 1597a (1 μ L) in SIM mode on Select PAH

Conclusion

The Select PAH column separated target PAHs in a complex mixture of coal tar in a single run with a runtime of 45 min. For eluting higher MW PAHs, a longer run time is necessary.

References

Beekman M., Boersma, A.H.R. and Sijm, D.T.H.M. (2008) Coal-tar pitch high temperature (CTPHT), transitional arrangements and way forward under REACH. REACH-SEA report of scoping study. Report 601780001/2008. National Institute for Public Health and the Environment, The Netherlands.

Bordajandi LR et al., (2008) Optimisation of the GC-MS conditions for the determination of the 15 EU foodstuff priority polycyclic aromatic hydrocarbons, J. Sep. Sci., 31, 1769-1778.

Gómez-Ruiz JA and Wenzl T, (2009) Evaluation of gas chromatography columns for the analysis of the 15+1 EU-priority polycyclic aromatic hydrocarbons (PAHs). Anal. Bioanal. Chem., 393, 1697-1707.

Lerda D, (2009) Polycyclic Aromatic Hydrocarbons (PAHs) Factsheet. European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, JRC 500871.

NIST. Standard Reference Material 1597a, Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar. National Institute of Standards and Technology, Gaithersburg, MD, USA.

Poster DL, Schantz, M.M., Sander, L.C. and Wise, S.A. (2006) Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods. Anal. Bioanal. Chem., 386, 859-881.

Sander LC and Wise SA, (1997) Polycyclic Aromatic Hydrocarbon Structure Index, NIST Special Publication. http://www.cstl.nist.gov/acd/839.02/pah/sp922_Search.htm. National Institute of Standards and Technology, Gaithersburg, MD, USA.

Wenzl T, Simon R, Kleiner J and Anklam E, (2006) Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union. Trends in Anal. Chem., 25(7), 716-725.

Ziegenhals K, Hubschmann HJ, Speer K and Jira W, (2008) Fast-GC/HRMS to quantify the EU priority PAH, J. Sep. Sci., 31, 1779-1786.

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Published in UK, April 12, 2011

SI02276



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