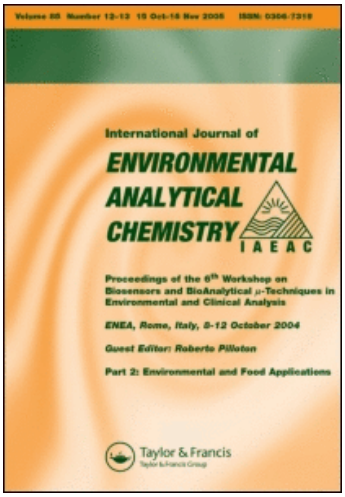

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New nano stationary phase GC capillary columns for fast analysis of PAH by GC and GC/MS

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New nano stationary phase GC capillary columns for fast analysis of PAH by GC and GC/MS†

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New nano stationary phase (NSP) capillary columns were evaluated for the analysis of 16 priority polycyclic aromatic hydrocarbons (PAH). To meet the regulatory requirements, the analytical procedures must provide adequate separation and identification of the 16 individual priority PAH. A 12 m conventional diameter NSP column provides fast separation of 16 priority PAH, meeting the USEPA regulatory requirements specified in method 610. The new NSP columns are selective and highly stable with a maximum operating temperature limit of 370°C. The columns have extremely low bleed at the standard working temperature of 325°C normally used for PAH analyses. Due to low bleed, these columns provide higher sensitivity for PAH in GC/FID and GC/MS analysis. Microbore columns with the NSP provide even faster analysis and ultra low bleed. In addition to the 16 priority PAH, the separation of benzo(e)pyrene and perylene from benzo(a)pyrene, and complete separation of dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, dibenzo[a,i]-pyrene, and dibenzo[a,h]pyrene, which are mandated for monitoring and analysis in food products by the European Food Safety Authority, is achieved on NSP columns. The fast analysis of 16 PAH in less than 6 minutes, repeatability over 200 runs, high temperature stability, and extremely low bleed illustrates the robust performance of NSP columns. Due to high selectivity, complete separation of 16 priority PAH was achieved on a very short (< 5 m) microbore NSP GC column. Fast analysis of 16 priority PAH on short NSP GC columns increases laboratory productivity and decreases laboratory operational costs. This is the first report on the application of selective, high temperature, extremely low bleed, NSP GC columns for PAH analysis.

Keywords: nano stationary phase; fast GC; priority PAH; high temperature column; microbore column

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a large group of organic compounds composed of two or more fused aromatic rings. Their properties, sources and analytical methods have been reviewed in the literature [1–4]. Hundreds of individual PAH persist in the environment. Over 600 individual PAH have been identified and their structural index, molecular weights, and preferred usage names are listed in the National Institute of Standards and Technology (NIST) special publication [5]. Due to their ecotoxicological relevance, unsubstituted PAH and thousands of substituted, mainly halogenated and

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alkylated PAH are environmentally important groups of compounds. The PAH are introduced into the environment through mainly two types of sources; natural and anthropogenic. Natural sources include forest fires, hydrothermal processes, and volcanic activities [6–9]. The main anthropogenic sources include industrial organic combustion such as waste incineration, coke, and crude oil processing at high temperatures, aluminium and carbon black production processes, motor vehicles fuel combustion, and residential wood burning [10–11]. Most of the anthropogenic processes are part of day-to-day activity of the industrialised world, and emissions of PAH through these sources will continue until processes with less emissions of PAH are developed. Human exposure to PAH occurs directly through air and water. Indirectly, humans are exposed to PAH through food products such as fish, sea food, and contaminated edible oil. PAH levels in air, water, soil, and food are monitored by numerous countries and international organisations with dedicated agencies, such as USEPA (United States Environmental Protection Agency), Environment Canada [12,13], World Health Organization [14] and European Commission [15]. Toxicity, carcinogenicity, and mutagenic properties of many PAH [16–18] are known. The USEPA have developed several test methods for the determination of PAH in municipal and industrial wastewater (Method 610), in solid waste (Method 8100) and in ambient air (Method TO-13A) [12,19,20]. The Ontario Ministry of the Environment monitors PAH in water using solid phase extraction and a Gas Chromatography/Mass Spectrometry (GC/MS) method [21].

Analysis of individual PAH in environmental, biological, and food samples is a very complex and laborious process. Sample analysis for PAH involves separation of PAH as a group from the sample matrix and then separation of individual PAH. Animal studies have revealed that individual PAH differ significantly in their adverse health/genotoxic effects. Gas chromatography with flame ionisation or mass spectrometer detection is generally the preferred analysis technique due to high resolution, selectivity, sensitivity, and ease of operation for complicated samples with a large number of PAH.

Determination of PAH in environmental or biological samples involves two main steps; sample preparation and analysis. There is some progress in automation of sample preparation procedures and use of techniques such as solid phase micro extraction and supercritical fluid extraction to reduce the sample preparation time. However, sample preparation procedures for complex environmental samples such as sediments or biological samples remains time consuming, laborious, and costly. There is tremendous advancement and improvement in analytical techniques for PAH, especially in GC analysis. Fused silica capillary column GC has become the method of choice due to numerous advantages such as high efficiency, high resolution, high sensitivity, and lower detection limits [22,23].

One of the difficulties associated with the determination of PAH in environmental and biological samples is the complexity of PAH mixtures in these samples. Individual PAH differ significantly in their toxicological properties. To assess the toxicity of a particular sample it is essential to separate and analyse individual PAH in the sample. Individual PAH, which differ in molecular weight, volatility, and polarity are generally analysed using conventional columns by GC. The capillary GC analysis exhibits very narrow peaks, but it is difficult to separate isomeric PAH using conventional stationary phase columns. For this reason, the minimum resolution requirement for some of the isomers is specified in USEPA Method 610.

Method validation for determination of 15 European Priority PAH in smoke condensates has been reported by 11 laboratories using a variety of conventional

GC columns of lengths 30 m to 60 m [24,25]. Various conventional and shape selective liquid crystal GC capillary columns have been used for the determination and certification of individual PAH including isomeric PAH in standard reference materials by the NIST [26,27]. In all of the methods developed by USEPA [12,19,20], conventional GC columns are used for the separation and analysis of PAH. Long (>30 m) conventional capillary columns with standard stationary phases provide separation of 16 priority PAH based on molecular weights, volatility and polarity with run times ranges between 20 and 60 minutes. Analysis of PAH in air, water, sediments, and food using conventional GC columns with run times from 20 to 60 minutes have been reported [28–31]. The term 'conventional' is used here for columns with an internal diameter (ID) of 0.25 mm or larger and lengths 25 m and longer. The use of conventional and microbore GC columns, and the advantages of microbore columns for fast analysis are reported [32].

Interest in fast GC analysis of PAH emerges from mandatory monitoring requirement of PAH in air, water, food products, sediments, and solid waste all over the world. Fast analysis of PAH meeting regulatory requirements results in fast turnaround time, increased throughput, increased laboratory productivity, increased accuracy by analysis of duplicate samples due to short runs, and decreased cost of analysis. Fast GC analysis is achieved using various techniques, such as fast temperature programming, fast carrier gas pressure programming, or both at the same time. It is also achieved using columns with smaller ID (microbore), using columns with thinner films, and using selective stationary phases. Fast GC analysis has been the focus of recent reviews [33,34]. Recently, published articles have shown theoretical aspects [35] and advantages of fast GC, such as increased sample throughput and possible increased precision due to the capability of running duplicate samples and more standards in the same time period [36–39].

Generally, fast GC is related to GC analysis using microbore columns. It is well established now that by reducing the ID and the length of the column, it is possible to maintain the same efficiency as a conventional long column and reduce the total analysis time by more than 50% without affecting the resolution. However, there are some limitations. If a conventional column cannot separate the desired components or if it takes a long time to separate them on the conventional column, then reduction in the ID and column length results in poor resolution of the desired components with fast GC. Applications of fast GC with conventional stationary phases for PAH analysis have been reported [40–42]. The separations of critical pairs on fast GC microbore columns with conventional stationary phases are not completely satisfactory.

Nano stationary phase has methyl and phenyl groups on the backbone siloxane. The composition is same as conventional stationary phase, for example 95% methyl and 5% phenyl groups on the backbone siloxane. The difference is that the nano stationary phase has low molecular weight, smaller molecular size, and shorter chain methylphenylpolysiloxane.

The nano size methylphenylpolysiloxane stationary phase is bonded to the capillary surface. Its higher selectivity compared to similar composition, but high molecular weight conventional stationary phase, is likely due to a specific orientation. Due to additional chemical bonding sites of nano size methylphenylpolysiloxane with the capillary surface, the thermal stability is high. In comparison, the conventional high molecular weight long chain polysiloxanes are vulnerable to decomposition to form and release cyclic polysioxanes at higher temperatures by a well known and documented backbiting mechanism [43].

Fast GC with short, shape selective liquid crystal columns, providing separation of critical pairs of priority PAH has been reported [44] to have an upper temperature limit of 285°C. The nano stationary phase columns have upper operating temperature limit of 370°C.

2. Experimental

A standard mixture of 16 regulated PAH at 2000 parts per million (ppm) and a standard mixture of 22 PAH including 16 regulated PAH and benzo(e)pyrene, perylene, dibenzo[a, l]pyrene, dibenzo[a, e]pyrene, dibenzo[a, i]pyrene, and dibenzo[a, h]pyrene at 200 ppm in dichloromethane were purchased from Ultra Scientific (USA) and used as stock solutions. The mixture of working standards of PAH was made from their stock solutions in GC grade dichloromethane. Fused silica capillary columns coated with new nano stationary phase (NSP-610) were obtained from J & K Scientific (Milton, Canada).

The following columns were evaluated for separation of PAH:

(1) NSP-610, 12 m × 0.25 mm ID × 0.10 μm film thickness.
(2) NSP-610, 10 m × 0.15 mm ID × 0.10 μm film thickness.
(3) NSP-610, 5 m × 0.10 mm ID × 0.10 μm film thickness.

An Agilent 6890 GC equipped with MSD (EI/PCI/NCI), FID and μECD, split/splitless EPC injectors and HP 5890 GC with FID were used for the separation and evaluation studies of the new NSP columns.

3. Results and discussion

The separation of 16 priority PAH on a new nano stationary phase (NSP) GC capillary column is shown in Figure 1. The critical pairs phenanthrene/anthracene (peaks 5 and 6), benzo(b)fluoranthene/benzo(k)fluoranthene (peaks 11 and 12), and indeno[1,2,3-cd] pyrene/dibenz[a, h]anthracene (peaks 14 and 15) are completely separated meeting the regulatory requirements of EPA Methods 610 and 8100. The new NSP column has remarkable selectivity for 16 priority PAH compared to other conventional stationary phase columns of similar or longer lengths. Fast temperature and pressure programming can be used to speed up the analysis but that is only possible for samples with wide boiling points [36]. Also, shorter length conventional columns can be used in fast GC of samples with a wide difference in boiling points. Fast GC of 16 PAH on short conventional ID columns is reported but the separation is not completely satisfactory, the critical pairs are not adequately separated [37]. The separation of close boiling compounds such as critical pairs in 16 priority PAH on the new NSP columns is impressive because it is achieved on a short length (12 m) and conventional ID (0.25 mm) column. This is the first report showing complete separation and fast GC of 16 priority PAH on a 12 m conventional ID (0.25 mm) column.

Highly polar and selective columns with polyethylene glycol (for fatty acid methyl esters), cyanopropyl polysiloxane (for PCB and Dioxins) and liquid crystal stationary phase (for PAH, Dioxins and PCB) show better selectivity for isomeric or close boiling compounds. However, the columns are less stable, have higher bleed at upper temperatures and have lower upper column operating temperature limits (<300°C). Analysis of high boiling or high molecular weight (HMW) compounds is problematic on

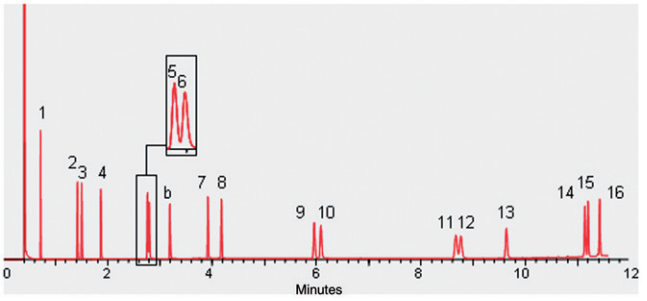

Figure 1. Fast GC of 16 priority PAH on an NSP conventional ID column.
Notes: Column: NSP-610, 12 m × 0.25 mm × 0.10 µm film thickness.
Chromatographic conditions
Temperature program: 120°C – 220°C @ 25°C/min. –240°C @ 4°C/min. –320°C @ 30°C/min. *Carrier gas*: helium. *Pressure*: 92.8 kPa. *Flow*: 2.1 mL/min. *Detector*: FID, 350°C. *Injector*: 220°C, split/splitless. *Sample*: 50 ppm PAH mixture.
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene, 9. Benz[a]anthracene, 10. Chrysene, 11. Benzo[b]fluoranthene, 12. Benzo[k]fluoranthene, 13. Benzo[a]pyrene, 14. Indeno[1,2,3-cd]pyrene, 15. Dibenz[a,h]anthracene, 16. Benzo[ghi]perylene, b. Carbazole.

polar columns, because these columns cannot be heated to higher temperatures; which are required for analysis of HMW PAH or removal of HMW contaminants from the sample after PAH analysis. In PAH analysis, high temperate stability of the column is important. Even after rigorous sample clean-up it is possible some HMW PAH and other compounds remain in the sample. The higher temperature limit (370°C) of a NSP column is advantageous because the column is useful for the analysis of HMW PAH in addition to 16 priority PAH, or to bake the column at higher temperatures to elute and clear-up the column from HMW PAH and other compounds.

The complete separation of 16 priority PAH with extremely low column bleed (<1 pA) was observed when the 16th PAH was eluted on NSP column (Figure 1). Because column bleed is extremely low in the retention time range of PAH elution time window, the detector sensitivity is high. Thus, there is a high signal to noise ratio and lower detection limits. Other advantages of fast analysis on conventional NSP columns is that the column can be used in any GC instrument without any modification, using standard parameters such as temperature programming and constant flow or pressure mode. Also, sample capacity is high and cool-on column injection is possible due to the conventional diameter. Fast analysis is achieved using helium carrier gas flow rate of 2.1 mL/min, which is suitable to use with GC/MS vacuum system without affecting sensitivity.

Fast GC analysis using advanced GC instruments or conventional GC with some modifications along with microbore columns is becoming popular. Fast GC implies reduction in GC analysis time by various means. It can be on short columns with or without smaller diameters (0.15 or 0.10 mm) compared to the analysis on conventional columns with 30 m or longer lengths and 0.25 mm or larger ID [32]. Desired separation and analysis in the reduced time is an important requirement associated with the fast GC. The selective stationary phases can make fast GC even faster. Generally, if the desired separation is achieved on a conventional ID column, then it is possible to achieve the fast separation on shorter microbore columns or better separation on the same length

microbore column (as that of a conventional column). In the current evaluation, the stationary phase is selective and fast GC is possible on a short length conventional ID column. Decreasing the column ID and length will result in elution of peaks in less time without affecting separation. The other two NSP-610 columns of lengths 10 m and 5 m, of IDs 0.15 mm and 0.10 mm (microbore) respectively, also were evaluated in the current studies. Fast GC separation and analysis can be achieved on columns with NSP simply by reducing the column length and ID due to the superior selectivity of the stationary phase. The critical pairs phenanthrene/anthracene, benzo(k)fluoranthene/benzo(b)fluoranthene, indeno[1,2,3-cd] pyrene/dibenz[a, h]anthracene are completely separated to meet the regulatory requirements of EPA Methods 610 and 8100. On the basis of the correlation of column length and ID of the column a 12 m conventional (0.25 mm ID) column will have a maximum number of theoretical plates equal to 56400 or 4700 plates/m, similarly a 10 m column of 0.15 mm ID will have theoretical plates equal to 79000 or 7900 plates/m. Further, using several conditions for fast GC such as increased inlet pressure, fast temperature programming will result in peaks to elute much earlier. The complete separation and fast GC of 16 priority PAH on a 10 m long NSP column of ID 0.15 mm is shown in Figure 2. The run time for analysis 16 priority PAH is 13 minutes and all 16 PAH are baseline-separated using standard GC conditions and parameters. In addition to 16 PAH, additional PAH such as benzo(e)pyrene and perylene are also separated from benzo(a)pyrene.

The complete separation of dibenzo[a, l]pyrene, dibenzo[a, e]pyrene, dibenzo[a, i]pyrene, and dibenzo[a, h]pyrene, which are mandated for monitoring and analysis in food products by the European Food Safety Authority, are achieved on this new column, as shown in Figure 2. To the best of our knowledge, this is the first report on the application of high temperature (370°C), short (<12m), conventional ID (0.25 mm) and microbore (0.15 mm IDs) GC columns providing complete separation of 16 priority PAH and additional PAH (benzopyrenes) specified in European Food Safety Authority.

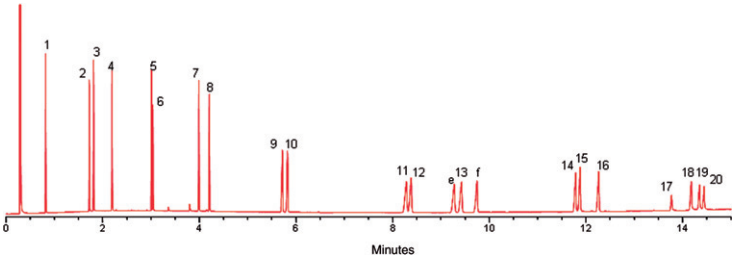

Figure 2. Fast GC of 22 PAH on an NSP conventional ID column.
Notes: Column: NSP-610, 10 m × 0.15 mm × 0.10 µm film thickness.
Chromatographic conditions
Temperature program: 100°C–220°C @ 30°C/min.–240°C @ 3°C/min.–320°C @ 15°C/min.
Carrier gas: helium. *Pressure*: 201.0 kPa. *Flow*: 1.0 mL/min.
Linear velocity: 57 cms/sec. *Detector*: FID, 350°C. *Injector*: 220°C, split/splitless.
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene, 9. Benz[a]anthracene, 10. Chrysene, 11. Benzo[b]fluoranthene, 12. Benzo[k]fluoranthene, e. Benzo[e]pyrene, 13. Benzo[a]pyrene, f. Perylene, 14. Indeno[1,2,3-cd]pyrene, 15. Dibenz[a, h]anthracene, 16. Benzo[ghi]perylene, 17. Dibenzo(a,l) pyrene, 18. Dibenzo(a,e)pyrene, 19. Dibenzo(a,i)pyrene, 20. Dibenzo(a,h)pyrene.

There are several reports on fast GC using conventional stationary phases in microbore columns (10 m × 0.10 mm ID) for analysis of 16 priority PAH. But reported separations are not completely satisfactory due to insufficient selectivity of the stationary phase and run times are longer than 10 minutes. Theoretically, a column with 0.15 mm ID is less efficient than column with 0.10 um ID with the same length [45]. However, due to higher selectivity, the NSP columns provide better separation even though they have less efficiency. In addition, the NSP column has high temperature stability up to 370°C. The separation under optimised conditions on this 10 m × 0.15 mm ID column is shown in Figure 3. The complete separation of 16 priority PAH occurs in less than 7 minutes. Such complete separation and fast GC of 16 priority PAH has not been reported on any other 10 m columns except shape selective liquid crystal columns [44]. The separation achieved is due to extraordinary selectivity of the NSP stationary phase and high resolution due to narrow ID. The NSP column with an ID of 0.15 mm can be used in any standard GC instrument up to 370°C.

Column stability is important for reproducible retention times and separations because environmental samples are associated with many other peaks eluting close to 16 priority PAH. If retention times change after a few sample runs in GC FID methods, then the set method will not be useful to determine the 16 PAH, because the other peaks eluting at PAH retention times will result in false positives. If GC/MS selected ion monitoring (SIM) method is used and if specified compounds are not eluted in a defined retention window due to column non-reproducibly will result in erroneous results. The chromatograms for run 1 and run 65 for 16 PAH injected under identical GC conditions are shown in Figure 4. Identical retention times after 65 runs is indicative of a highly reproducible GC column. Further studies of over 200 runs shows little change in retention times for 16 PAHs on this column. Low column bleed of 0.5 pA at high temperature and stability up to 370°C of NSP can be due to bonding of low molecular weight and smaller size molecules of the NSP resulting in less decomposition of the stationary phase.

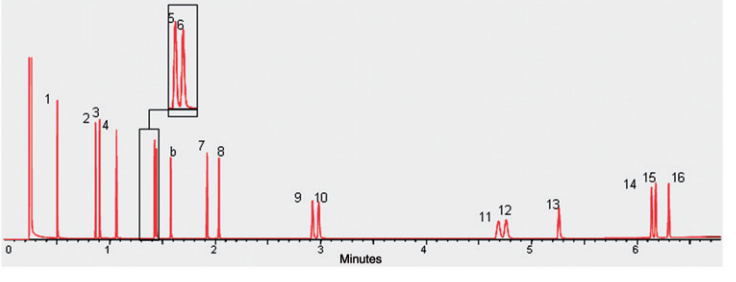

Figure 3. Fast GC of 16 priority PAH on an NSP conventional ID column using optimised conditions.
Notes: Column: NSP-610, 10 m × 0.15 mm × 0.10 μm film thickness.
Chromatographic conditions
Temperature program: 100°C–220°C @ 100°C/min.–223°C @ 1°C/min.–300°C @ 50°C/min. (3).
Carrier gas: helium. *Pressure*: 600.0 kPa. *Flow*: 1.5 mL/min. *Detector*: FID, 350°C, *Injector*: 220°C, split/splitless. *Sample*: 20–50 ppm PAH mixture.
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene, 9. Benz[a]anthracene, 10. Chrysene, 11. Benzo[b]fluoranthene, 12. Benzo[k]fluoranthene, 13. Benzo[a]pyrene, 14. Indeno[1,2,3-cd]pyrene, 15. Dibenz[a,h]anthracene, 16. Benzo[ghi]perylene, b. Carbazole.

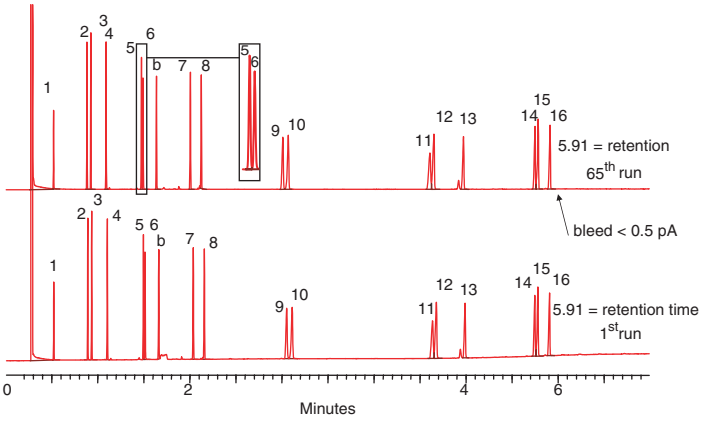

Figure 4. Fast GC of 16 priority PAH on an NSP conventional ID column showing reproducible results.
Notes: Column: NSP-610, 10 m × 0.15 mm × 0.10 μm film thickness.
Chromatographic conditions
Temperature program: 120°C–220°C @ 100°C/min.–223°C @ 1°C/min.–320°C @ 50°C/min. (3).
Carrier gas: helium. *Pressure*: 600.0 kPa. *Flow*: 1.5 mL/min. *Detector*: FID, 350°C, *Injector*: 220°C, split/splitless. *Sample*: 20–50 ppm PAH mixture.
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene, 9. Benz[a]anthracene, 10. Chrysene, 11. Benzo[b]fluoranthene, 12. Benzo[k]fluoranthene, 13. Benzo[a]pyrene, 14. Indeno[1,2,3-cd]pyrene, 15. Dibenz[a,h]anthracene, 16. Benzo[ghi]perylene, b. Carbazole.

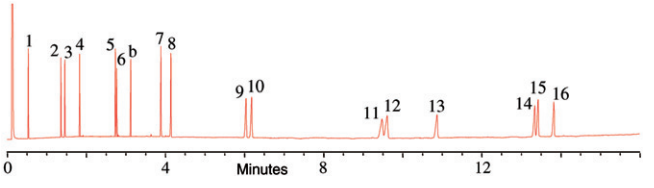

Figure 5. Fast GC of 16 priority PAH on a new NSP microbore column using standard GC conditions.
Notes:
Column: NSP-610, 5 m × 0.10 mm × 0.10 μm film thickness.
Chromatographic conditions
Temperature program: 120°C–220°C @ 25 C/min.–235°C @ 2°C/min.–350°C @ 15°C/min.
Carrier gas: helium. *Pressure*: 600.0 kPa. *Flow*: 1.5 mL/min. *Detector*: FID, 350°C, *Injector*: 220°C, split/splitless. *Sample*: 50 ppm PAH mixture.
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6. Anthracene, 7. Fluoranthene, 8. Pyrene, 9. Benz[a]anthracene, 10. Chrysene, 11. Benzo[b]fluoranthene, 12. Benzo[k]fluoranthene,13. Benzo[a]pyrene, 14. Indeno[1,2,3-cd]pyrene, 15. Dibenz[a,h]anthracene, 16. Benzo[ghi]perylene, b. Carbazole.

Complete separations of 16 PAH were also achieved on a very short (5 m) micro-bore column with ID 0.10 mm as shown in Figure 5. A 5 m microbore column has a very small sample capacity that results in overloading the column with 20 ppm sample. In spite of overloading, it is notable that due to high selectivity, separation of critical pairs in the 16 priority PAH mixture is achieved on such a short column (5 m). This is not possible

and has not been reported in the literature to date on any other column of similar dimensions.

4. Conclusions

New nano stationary phase columns are highly selective for separation and analysis of 16 Priority PAH of EPA Method 610 and dibenzopyrenes of EC protocol. Due to their extraordinary selectivity for 16 priority PAH, short NSP columns (<12 m) with IDs 0.10 mm, 0.15 mm, and 0.25 mm, provide fast analysis, which increases laboratory productivity. Nano stationary phase columns have extremely low bleed, and an operating temperature range of 0 to 370°C. Enhanced selectivity, high temperature stability, and reproducibility for fast analysis of PAH on NSP columns equates to robust analytical performance for GC and GC/MS methods.

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