Development and Application of Isomer Specific GC Capillary Columns for PAH and PCDD Analysis

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Introduction

The current methods of polycyclic aromatic hydrocarbons (PAH) determination in environmental samples involve the use of capillary gas chromatography (GC)[1-7] or high performance liquid chromatography (HPLC) [8-11] techniques. GC is a simple and less-expensive method for the determination of PAH. The use of GC/MS in selected ion monitoring (SIM) mode can provide positive identification and lower detection limits of PAH in complicated environmental samples. The U.S. Environmental Protection Agency (USEPA) has listed 16 polycyclic aromatic hydrocarbons (PAH) as priority pollutants in Method 610. Accurate determination of the 16 PAH can only be possible when all components are completely separated. Quantitation of regulated PAH and toxicity assessments based on analytical results with incomplete separation of PAH may be questionable and misleading. The required baseline separation of the 16 PAH depends largely on column selectivity. Traditionally the analysis of PAH including the 16 priority PAH is performed using conventional GC capillary columns. The time required to do analysis varies from 30 to 60 minutes.[7, 12-13] Also, the separation of isomeric PAH is very difficult or impossible on conventional capillary columns. To overcome these difficulties, an isomer specific capillary column is investigated for separation and stability. The analysis of polychlorinated dibenzo-p-dioxins, especially the highly toxic 2,3,7,8-chloro-substituted dioxin, is also very difficult using conventional capillary columns. Often, long columns are necessary to achieve the separation of 2,3,7,8-chlorinated dibenzo-p-dioxins (2,3,7,8-CDD) from other PCDD isomers. A fast and reliable GC column for their separation and quantitation is investigated.

Materials and Methods:

A standard mixture of 16 regulated PAH at 100 parts per million (ppm) per component (in dichloromethane) from Ultra Scientific (USA) was used. Diluted working standards were prepared from the stock standard solution. An ICB-PAH and LC-50 columns were prepared using isomer specific stationery phases and static coating procedures.[1] An ICB-PAH column,12 m X 0.25 mm, 0.15 µm film, LC-50 Columns, 10 m x 0.15 mm x 0.10 µm and 10 m x 0.15 mm x 0.10 µm were prepared and used in this investigation. 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 studies of PAH and PCDD. An ICB-5 column, with conventional non polar stationary phases were used for the separation comparison

Result and Discussion

The ICB-PAH and LC-50 columns made using polymeric liquid crystal stationary phases have shown superb isomer specific selectivity for PAH and PCDD separations. GC conditions and parameters were studied to optimize the separation of regulated 16 PAH specified in the USEPA Method 610 It was shown that analysis using isomer specific stationary phase column can be completed in less than 15 minutes with base line separation of all 16 PAH. Injection of the PAH mixture over 60 times on ICB-PAH column did not show any change in performance of the column for separation or retention time. Overlapped GC chromatograms for 16 PAH for the first run and the 60th run are shown in **Figure 1.** To make the separation even faster conditions were developed using higher column head pressure, which gives analysis of 16 PAH in less than 10 minutes. Critical pairs/isomeric PAH such as phenanthrene/anthracene, benzo(b)fluoranthene/benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene/dibenzo(a,h)anthracene are completely resolved on this ICB-PAH column meeting the specified criteria of the USEPA Method 610. For unambiguous detection and quantitation, complete separation of the regulated 16 PAH is essential. It is also crucial that other isomeric PAH are completely separated from the regulated 16 PAH. For example, accurate amounts of three PAH in the list of 16 PAH, namely chrysene, benzo(a)pyrene and benzo(a,h)anthracene cannot be determined unless it is confirmed that they are

not co-eluting with isomeric compounds triphenylene, perylene and dibenzo(a,c)anthracene, respectively. From published work and retention index values, it is evident that these isomeric PAH are difficult or impossible to separate on conventional non-polar capillary columns. In addition, it is also confirmed that other isomeric PAH do not co-elute with the 16 priority PAH. To confirm the separation of these isomeric PAH from regulated PAH, a mixture of an additional 10 PAH was prepared and analyzed on an ICB-PAH column. All 26 PAH including 16 regulated PAH were separated on this column. More specifically, chrysene is separated from benzo(a)anthracene and triphenylene; benzo (b)fluoranthene is separated from benzo(k)fluoranthene; benzo(a)pyrene is separated from benzo(e)pyrene and perylene , and benzo(a,h)anthracene is separated from benzo(a,c)anthracene. With most columns, it would require a 40 to 60 minute run time for the baseline separation of 16 PAH using non-polar columns. The major advantage of the ICB-PAH column is, that it can be used in any conventional capillary GC for reproducible and reliable quantitative analyses of PAH. Column bleed, a common problem in capillary column GC, restricts the use of columns in GC and GC/MS for trace analysis. The ICB-PAH column has less than 5 pico-amperes (pA) of column bleed at its upper operating temperature of 285°C which makes it highly stable isomer specific column compared to other isomer specific capillary columns. The column was also heated at 100°C/min to see the effect of temperature programming on the column bleed. A consistent column bleed (<5 pA) was observed.

Also, the separation of 2,3,7,8-substituted chlorinated dioxin isomers from the other isomers and analysis of mono- to octachlorodibenzo-p-dioxins was achieved in less than 27 minutes using isomer specific LC-50 column, **Figure 2**. The columns were tested for selectivity, temperature stability, and longevity. The isomer-specific ICB-PAH and LC-50 columns provided fast analysis of 16 priority PAH and chlorinated dioxins as compared to the columns with traditional non-polar stationary phases.

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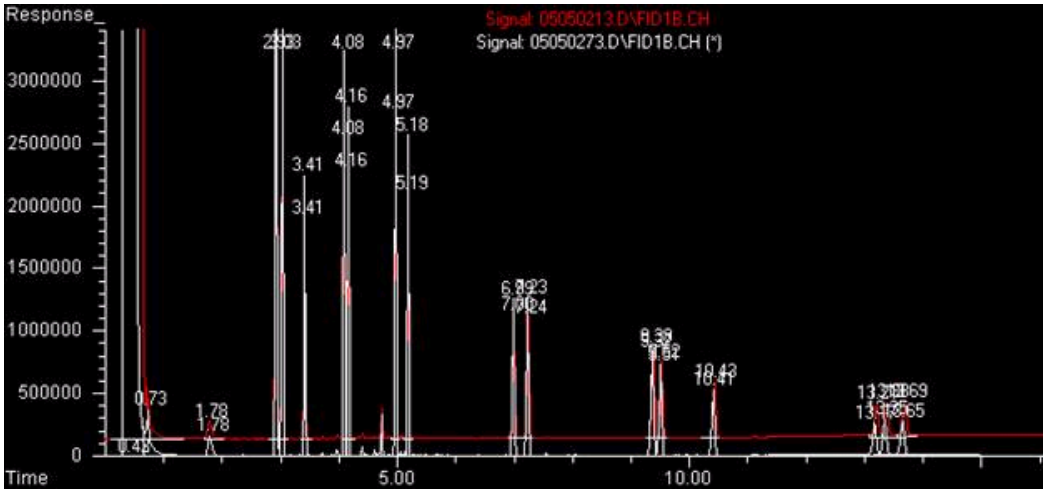

Figure 1: Separation of USEPA Method 610 PAH on ICB -PAH Column. Upper chromatogram, 1st run; lower chromatogram, 60th run. Column: ICB PA, 12 m x 0.25 mm x 0.15µm film thickness.

Chromatographic conditions: Temperature program: 120^{0}C for 1 min., to 220^{0}C @ 40^{0}C/min, to 270^{0}C @ 5^{0}C/min, 5 min at 270^{0}C.

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.Dibenzo[a,h]anthracene,16.Benzo[ghi] perylene

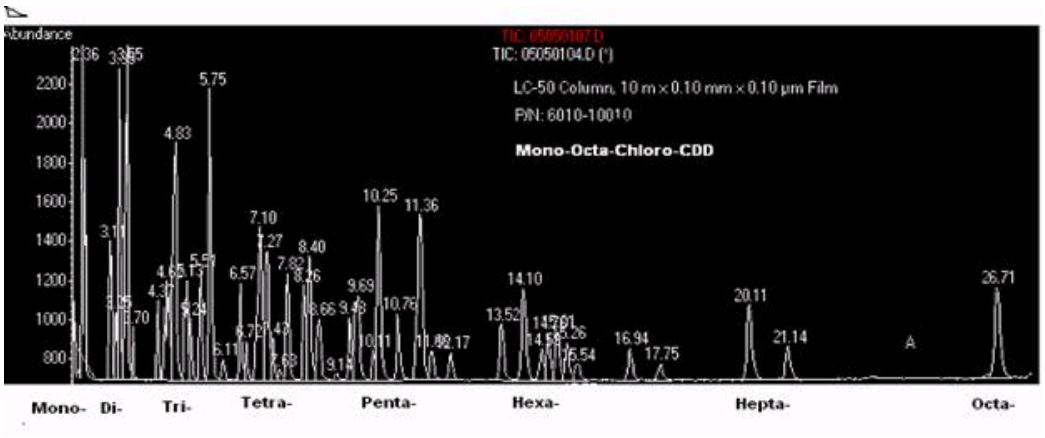

Figure 2: GC/MSD/EISIM TIC for mono -to octa-chlorodibenzo-p-dioxins. One ion (M+2 or M+4) for each mono - to octa-chlorodibenzo-p-dioxin congener was monitored. Chromatographic conditions: Oven Temperature 100 ^{0}C, programmed to 170^{0}C @ 40^{0}C/min-270^{0}C @3 ^{0}C/min, 10 minutes at 270^{0}C.