‘Automated On-Line LC-GC for the Clean-Up and Determination of PAH in Urban Air[1]

LC

Varian Application Note

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of compounds that have received considerable attention owing to their mutagenic and carcinogenic properties. Because PAH are synthesized during the incomplete combustion of organic materials, they are often present in vehicle emissions, fire smoke, and airplane exhausts. Environmental monitoring of our urban air, water, and soils for PAH is an ongoing concern.

In this application, a fully automated system, comprising high performance liquid chromatography (LC) coupled on-line to gas chromatography (GC), was constructed for the analysis of PAH in urban air particulate extracts. Each extract was pre-separated into ring-size PAH fractions by automated analytical LC, and a 1000-µL LC fraction was then transferred on-line to the GC which resolved the individual PAH present in that fraction. For several reasons, pentane was selected as the LC mobile phase. **Although reciprocating pumps from six different vendors were evaluated, only the Varian 9000 Series pump was able to deliver a constant flow of pentane.** Transfer of the fraction from the LC to the GC was achieved via a loop-type interface, using a concurrent solvent evaporation technique [CSE (2)] and an early solvent vapor exit.

Experimental

Sample Preparation: (1) Standard PAH mixture: The LC-GC system was calibrated using a quantitative PAH standard solution (each at 50-100 pg/µL). (2) Urban air: A 325-m^3 sample of ambient street air was collected with a high volume sampler. Particulate and semi-volatile fractions were trapped on a glass fiber filter and two polyurethane foam plugs connected in series. Internal standard was added to the filter and plugs, which were then Soxhlet-extracted with dichloromethane for 24 hours. The extracts were vacuum reduced to 1 mL at 30°C, after which 200 µL of each extract was pre-separated on a 60 mm x 6 mm i.d. column packed with 10% deactivated silica. Paraffinic, olefinic, and aromatic compounds were eluted with 6-mL cyclohexane, thereby removing unwanted particles and polar compounds.

LC: A schematic diagram of the LC-GC system is shown in **Figure 1**. A Varian 9001 LC pump was used to pump LC grade pentane at 1 mL/min from a 5-L reservoir, in which the solvent was degassed by (and over-pressurized with) helium. A µ-Bondapack-NH$_2$ aminopropylsilane analytical LC column was used via a 4-port switching valve (SW1). Flow of mobile phase through the column could be reversed by switching this 4-port valve. Samples were transferred to the column from a Varian Marathon AutoSampler containing a Rheodyne injection valve with a 100-µL injection loop.

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[1] Abstracted from Reference (1) with permission.

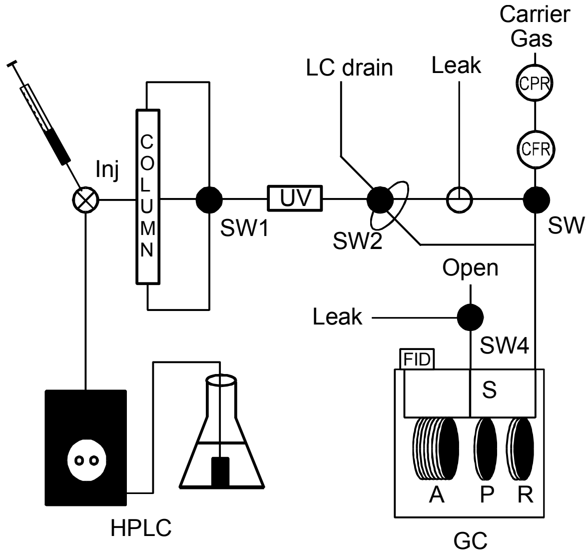

Figure 1. Schematic diagram of the LC-GC system[2]

Aromatic compounds eluting from the LC column were detected by an on-line UV detector operated at 254 nm, and the detector outlet was connected to the LC-GC interface.

LC-GC Interface: The LC-GC interface was a carrier gas control unit, a loop interface, and a GC injection unit. The carrier gas control unit consisted of a constant pressure regulator (CPR), and a constant flow regulator (CFR) coupled in series. The loop interface (SW2) was a 6-port valve with a 1000-µL stainless steel loop. By switching the valve, either the LC eluate or the GC carrier gas could be directed through the loop. Valve 3 (SW3) selected the carrier gas flow either through the loop interface, or directly to the GC retention gap. The connecting lines from SW2 and SW3 to the retention gap were 0.5 m x 0.32 mm i.d. fused silica. A leak was inserted between SW2 and SW3, flushing any remaining solvent vapors from the connecting lines when the interface was not in the injection mode.

The GC injection unit was a 3 m x 0.53 mm uncoated fused silica retention gap (R), connected to both SW2 and SW3 by a glass press-fit connector glued with epoxy resin. The retention gap was led through an empty, unheated injector seat into the GC oven, where its other end was connected to a 2 m x 0.32 mm i.d. precolumn (P) internally coated with 0.25-µm 5% phenyl polydimethylsiloxane gum (DB-5). The outlet of the precolumn was connected both to the analytical column (A) and to a 0.2 m x 0.53 mm uncoated fused silica vapor exit (V) by means of a glass press-fit T-piece connector glued with epoxy resin.

The solvent vapor exit passed from the GC oven through the empty injector seat and connected to a switching valve (SW4). The outlet from the solvent vapor exit could then be switched between an open line or a restrictor (1.0 m x 0.05 mm i.d. fused silica), which strongly reduced the flow through the solvent vapor exit.

GC: A Varian 3700 GC with hydrogen carrier gas and a flame ionization detector (FID) was used. The analytical GC column was a 28 m x 0.32 mm i.d. open tubular column internally coated with 0.25-µm DB-5. The oven temperature was maintained at 54°C for two minutes after injection and then programmed linearly at 7°C per minute to 300°C, with a 10 minute hold.

Results

Optimization of the LC-GC System: The LC-GC system was operated with standard analytical LC columns in order to provide high sample capacity. With mobile phase flow rates of 1 mL/min, it was possible to use a standard reciprocating LC pump. Pentane was chosen as the mobile phase to avoid losing the 3-ring PAH during LC-GC transfer with CSE due to co-evaporation with the mobile phase. The lower the boiling point of the LC mobile phase, the fewer volatile sample components will be lost. However, finding a reciprocating LC pump that could pump pentane successfully was difficult. **Reciprocating pumps from six different vendors were evaluated, but only the Varian 9000 Series pump was able to deliver a constant flow of pentane.** The Varian pump's success was attributed to the special construction of its mechanical inlet valve, which avoids the cavitation problems of typical “ball-and-seat” inlet check valves.

Normal phase LC was used to separate PAH according to ring size. A single peak containing PAH with three (or more) rings was obtained by backflushing the column just prior to the elution of anthracene. LC-GC analysis of the calibration solution containing 19 PAH was performed first. This established retention times for peak identification and correction factors for calculations of concentrations from the automated clean-up and analysis procedure. The correction factors included relative yield in the LC clean-up, relative transfer yield from LC to GC, and a response factor for the calibration system. The detection limit of individual PAH for the LC-GC system was determined to be approximately 1 ng per sample at a signal-to-noise ratio of 3:1.

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[2] Reproduced from Reference (1) with permission.

Analysis of Urban Air Samples: Cyclohexane extracts of the particulate and semi-volatile fractions of the urban air sample were transferred to vials and placed in the LC autosampler rack. Four automated LC-GC analyses were performed on each sample. **Figure 2** shows the LC chromatogram of the semi-volatile fraction. The backflush peak eluting at 22 minutes was transferred into the GC by the loop interface using the CSE technique. GC analysis of the semi-volatile fraction was then performed on-line (**Figure 3**). Similarly, the GC chromatogram obtained by LC-GC analysis of the particulate fraction of urban air is shown in **Figure 4**. Results of the four replicate LC-GC analyses for each fraction are given in **Table 1**; %RSD for this method was usually less than 7%.

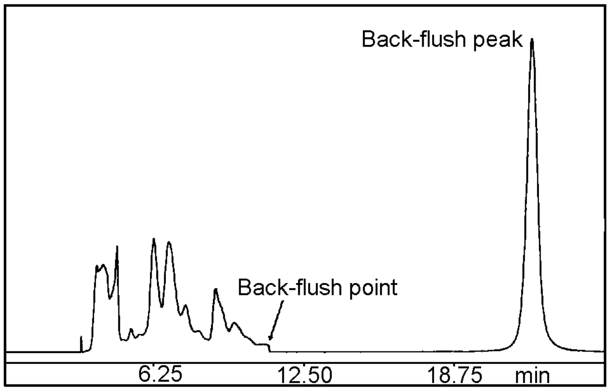

Figure 2. LC chromatogram from the LC-GC analysis of the semi-volatile fraction of the urban air sample. The corresponding gas chromatogram is shown in Figure 3.[2]

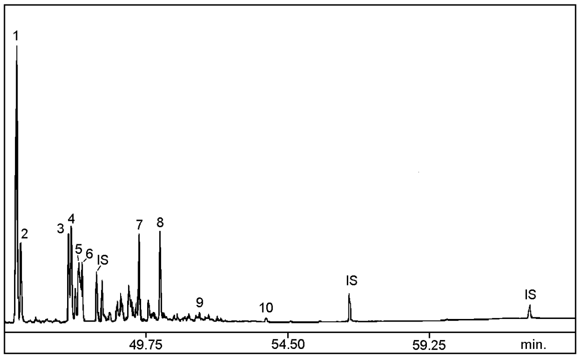

Figure 3. Gas chromatogram of the LC-GC analysis of the semi-volatile fraction of the urban air sample. The corresponding liquid chromatogram is shown in Figure 2. Peak numbering as in Table 1[2]**.**

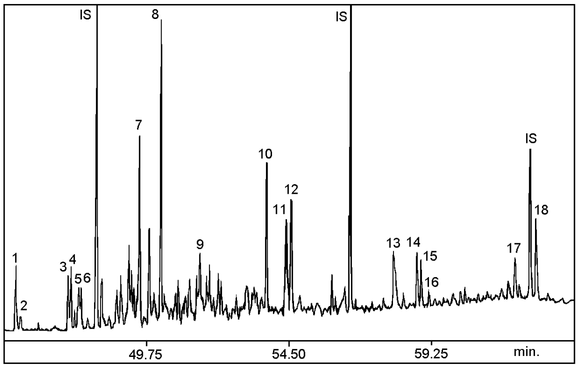

Figure 4. Gas chromatogram from the LC-GC analysis of the particulate fraction of the urban air sample. Peak numbering as in Table 1[2]**.**

Table 1: Concentrations of 19 PAH in samples of urban air (4 replicate analyses).[2]

		Particulate a)		Semi-vol c)	
No.	**Compound**	**ng/m^3**	**%RSD b)**	**ng/m^3**	**%RSD**
1	Phenanthrene	1.5	1.3	80	5.1
2	Anthracene	0.3	11	14	4.9
3	3-Methylphenanthrene	0.7	3.3	15	2.1
4	2-Methylphenanthrene	1.0	1.7	16	6.9
5	9-Methylphenanthrene	0.6	1.8	11	2.4
6	1-Methylphenanthrene	0.7	1.5	8.7	10.1
7	Fluoranthene	2.4	1.1	12	3.7
8	Pyrene	3.4	4.2	13	3.1
9	Benzo(a)fluorene	1.3	1.9	1.8	2.6
10	Benzo(ghi)fluoranthene	2.8	2.8	0.8	6.7
11	Benz(a)anthracene	1.5	1.5	n.d. d)	-
12	Chrysene	2.1	1.9	n.d.	-
13	Benzo(k+j)fluoranthene	1.0	14.8	n.d.	-
14	Benzo(e)pyrene	1.3	1.4	n.d.	-
15	Benzo(a)pyrene	1.1	3.3	n.d.	-
16	Perylene	0.3	1.2	n.d.	-
17	Indeno(1,2,3-cd)pyrene	1.4	2.6	n.d.	-
18	Benzo(ghi)perylene	3.0	1.7	n.d.	-
19	Coronene	2.0	6.3	n.d.	-

a) particulate fraction from urban air sample
b) relative standard deviation
c) semi-volatile fraction from urban air sample
d) not detected (<0.1 ng/m^3)

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Conclusions

On-line LC-GC provides a fully automated method for the clean-up and analysis of PAH in environmental samples. Compared with ordinary off-line LC clean-up followed by GC analysis, sensitivity was increased 50-100 fold, giving a detection limit of a few nanograms per PAH by FID. The total time required for clean-up and analysis was only 1.5 hours, most of which did not require human attention. The sensitivity, precision, and automation of this technique makes it a very useful tool for the analytical chemist.

References

1. Conny Östman, Agneta Bemgård, and Anders Colmsjö, HRC 15 (1992) 437-443.

2. K. Grob, On-Line Coupled LC-GC, Hüthig, Heidelberg, Germany (1991).