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ISOLATION AND HARVESTING OF INDIVIDUAL PAHs BY A PREPARATIVE CAPILLARY GAS CHROMATOGRAPHY SYSTEM: OPTIMIZATION OF THE INSTRUMENTAL CONDITIONS

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Introduction

The field of compound-specific isotope analysis (CSIA) is rapidly growing since it can provide information about the source of individual compounds[1,2] and the (kinetic isotope fractionating) processes that chemicals may undergo in the environment[3]. The development of methods to promote the efficient harvesting of individual compounds could expand CSIA to isotopes of low natural abundance and overcome the current prohibitively large sample size requirement.

A technique that holds promise to meet this analytical need is automated preparative capillary gas chromatography (PCGC) which has only recently become commercially available. The potential of PCGC system was initially demonstrated by harvesting individual alkanes and fatty acids from archaeological samples followed by measurement of their ^{14}C content using accelerator mass spectrometry[4]. The ^{14}C age of the individual compounds was then calculated. The same PCGC system has recently been used in several other studies[1,2] including harvesting of individual PAHs from environmental standard reference materials followed by successful measurement of their compound-specific ^{14}C abundance.

Even if the PCGC system has systematically been used for the isolation of individual compounds, the harvesting efficiency as a function of compound properties and an optimizing scheme of the PCGC-specific operating parameters has never been thoroughly reported. The objective of the present study was to optimize several instrumental parameters of the PCGC system in order to achieve the optimal trapping efficiency of individual PAHs.

PAHs were selected as target compounds because of the interest in elucidating the sources of these carcinogenic chemicals to the urban atmosphere and other ecosystems. It was recently demonstrated that radiocarbon dating of individual PAHs (requiring PCGC) is ideal for discriminating between PAH combustion sources using fossil fuel (^{14}C-free) versus those stemming from modern biomass (contemporary ^{14}C)[2]. The present work demonstrates that several operating parameters must be properly adjusted in order to obtain high recoveries of PAHs during PCGC harvesting. The increase of the recoveries not only minimizes the risk of instrument-induced isotope fractionation but is also crucial when samples of low PAH content are going to be subsequently analysed by accelerator mass spectrometry.

Methods and Materials

The PCGC system used is shown in Figure 1. Briefly, the organic mixture containing the compounds under investigation is repeatedly injected by an autosampler into the gas chromatography system equipped with a Cooled Injection System (CIS) and a “megabore” capillary column. The end of the column is attached to a zero dead volume effluent splitter that

diverts a portion of the effluent to the detector while the majority is transferred to and trapped in a preparative fraction collector (PFC) unit.

To optimize the PCGC performance, the following six instrumental parameters were investigated: CIS splitless time, CIS solvent venting time, CIS "stop flow" mode, CIS injection rate, PFC switch temperature and PFC trapping temperature. A series of injections of the SRM 2260 solution (mixture of 24 PAHs) were made in order to investigate the signal intensity of each PAH by varying each one at a time of the instrumental parameters cited above. For each series of injections, the instrumental parameter under investigation was gradually increased and the peak area of each PAH was integrated.

Results and Discussion

Volatile PAHs (Molecular Weight "MW " between 128 and 170) and PAHs of intermediate volatility (MW 178-202) provided a quite stable signal during the variation of splitless time between 20 and 150 s (Figure 2a). However, the peak areas of the less volatile PAHs (MW 228-278) were sharply decreased to 20% when the splitless time was set lower than 30 s. Based on above results, a splitless time of 60 s was chosen as the optimum value for PAHs.

An increase of solvent venting time caused a sharp decrease of the signal of the more volatile PAHs (MW 128-154) and a less steep decrease for PAHs of intermediate volatility (MW 170-178) (Figure 2b). The less volatile PAHs (MW 192-276) did not exhibit a significant decrease even for solvent venting time of 2 min. Therefore, a solvent venting time of 5 s was chosen as the optimum value for the harvesting of PAHs by PCGC. In addition, Figure 3a shows that the PCGC performance should be inferior when the CIS injector operates in "stop flow" mode (SF), especially for the more volatile PAHs.

The injection rate is known to significantly affect the chromatography when the sample is introduced by hot split or splitless techniques. In the present study the SRM 2260 solution was injected in CIS injector in both fast (FI) and slow mode (SI). Figure 3b shows that a lower injection rate causes a significant discrimination even when the PAHs are injected in a cold CIS inlet. Therefore, the maximum injection speed should be selected during harvesting of PAHs by a PCGC system equipped with a CIS injector.

The recoveries of Fluoranthene, Pyrene, Retene, and Chrysene during PCGC harvesting were not dependent on switch temperature. On the contrary, the recovery of Fluorene exhibited a significant decrease when the switch temperature increased from 280 to 340 ^{o}C, while the opposite trend was observed for the less volatile Perylene (Figure 4a). The low recovery for Fluorene could be attributed to both thermal decomposition and evaporation losses. Overall, our results suggest that higher temperatures should be set at the PFC switch when less volatile PAHs are going to be harvested. In this study, a switch temperature of 340 ^{o}C was selected as the optimum value. The recoveries of PAHs as a function of trapping temperature are also presented in figure 4b. In general, high recoveries of 90-100% were obtained for Fluoranthene, Pyrene, Retene and Chrysene as well as for Perylene at all trapping temperatures. However, the recovery of Fluorene was about 50% at –16 and 0 ^{o}C and even below 40% at 30 ^{o}C.

After the optimization, the overall performance of the PCGC system was evaluated (Table 1). A high reproducibility was evident for both the retention time and signal intensity of the PAHs, indicating the excellent performance of the CIS inlet. With the exception of Fluorene, the average recoveries for all other PAHs were excellent during PCGC harvesting and ranged between 90%

and 100%. Furthermore, the average purity of the PAHs harvested by PCGC ranged between 97% and 100% (see Table 1). This is the first study to systematically optimize the performance of such a system and the results will facilitate a broader application of preparative capillary gas chromatography for various applications, including radiocarbon analysis of individual PAHs.

Table 1: Overall performance of PCGC system against PAHs, after optimization procedure.

Compound	Retention time (min)	Peak Area (10^7 counts)	Recovery %	Purity %
Fluorene	18.971 ± 0.014	5.4 ± 0.4	47.0 ± 4.7	98.5 ± 0.7
Fluoranthene	31.567 ± 0.014	4.1 ± 0.3	88.3 ± 3.6	99.9 ± 0.1
Pyrene	33.056 ± 0.012	4.3 ± 0.3	89.3 ± 3.9	98.2 ± 2.5
Retene	34.910 ± 0.013	2.6 ± 0.2	91.0 ± 4.3	97.7 ± 1.3
Chrysene	41.912 ± 0.018	3.8 ± 0.3	94.2 ± 5.6	96.6 ± 2.0
Perylene	59.323 ± 0.035	3.5 ± 0.2	102.4 ± 7.2	97.8 ± 1.7

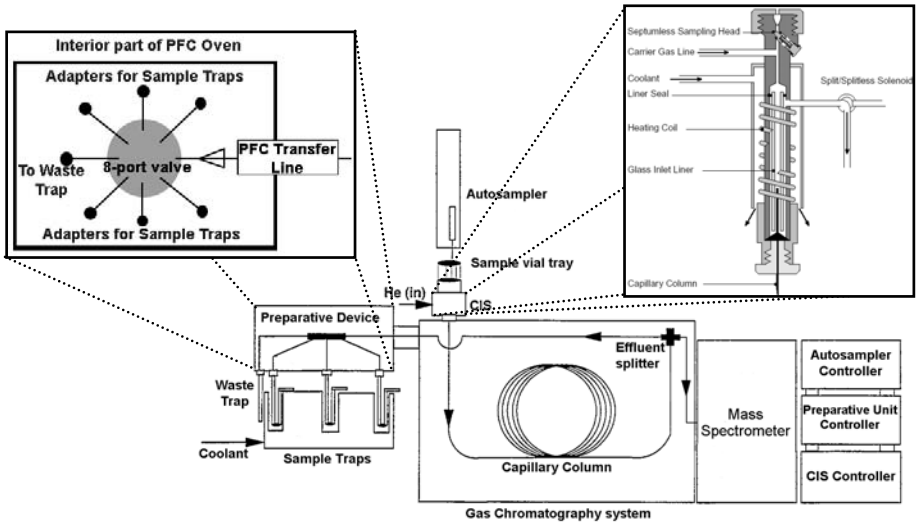


Figure 1: Schematic diagram of preparative capillary gas chromatography system

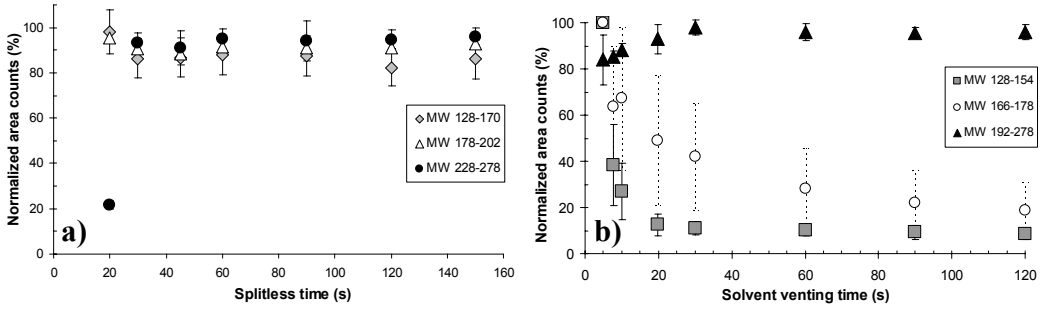


Figure 2: Relative area counts for three molecular-weight categories of a total of 24 PAHs as a function of a) splitless times and b) Solvent venting time. *The area counts measured for each category were normalized against the maximum value observed during the corresponding injection series.*

Figure 3: a) Ratio of area counts observed when the "stop flow" (SF) feature was enabled, divided by the corresponding area counts measured when the column flow was not stopped (F), b) Ratio of area counts observed when the sample was injected in slow mode (SI), to the corresponding area counts measured when the injection was performed in fast mode (FI).

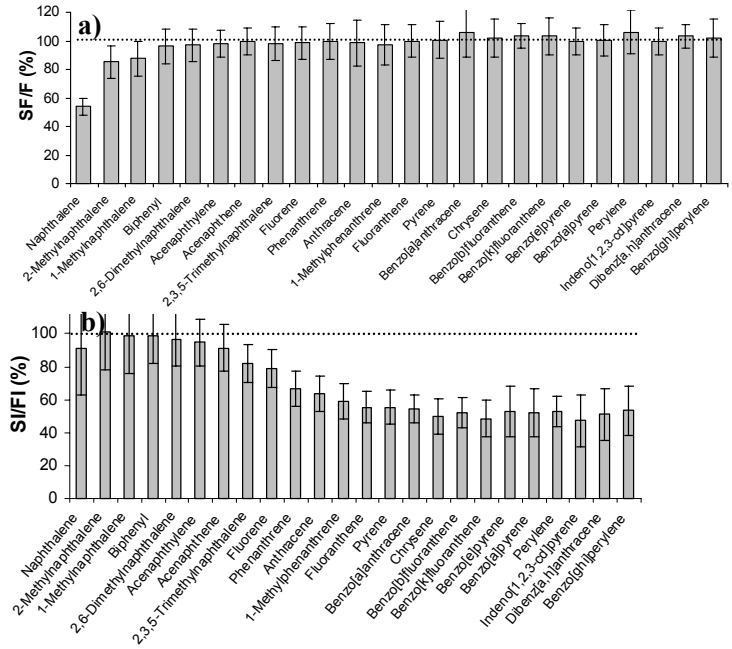
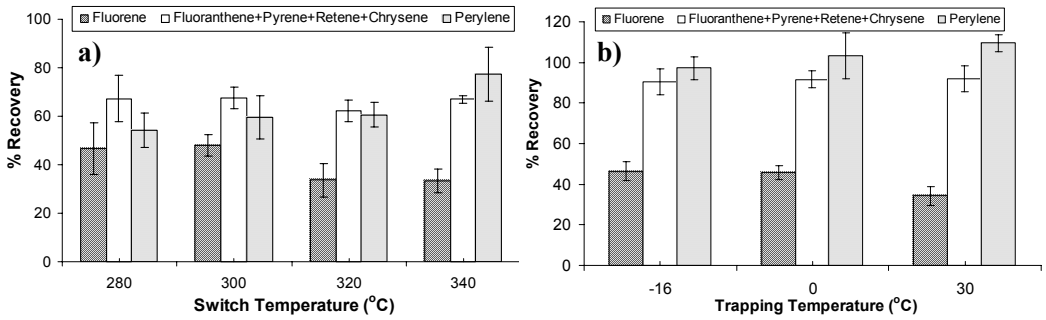


Figure 4: Trapping recovery of PAHs as a function of a) switch temperature and b) trapping temperature of the preparative fraction collector.



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