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Optimization of a preparative capillary gas chromatography–mass spectrometry system for the isolation and harvesting of individual polycyclic aromatic hydrocarbons

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Abstract

Operation parameters of a preparative capillary gas chromatography (pcGC) system were optimized to facilitate clean and efficient harvesting of individual polycyclic aromatic hydrocarbons (PAHs) for subsequent compound-specific radiocarbon analysis. For PAHs, the recommended optimized settings of the specially-designed pcGC cooled injection system (CIS) and preparative fraction collector (PFC) are: 5 s CIS solvent venting time, deactivation of CIS ''stop flow'' injection mode, autoinjector ''fast injection'' mode, 60 s CIS splitless time, 340 °C PFC switch temperature, and 30 °C (ambient) trapping temperature. These optimized conditions yielded highly reproducible, pure, and efficient pcGC harvesting of six PAHs with mass recoveries of 90–100% and purity of the isolates of 97–100%.

Keywords: Preparative chromatography; Instrumentation; Injection methods; Polynuclear aromatic hydrocarbons

1. Introduction

Many novel research questions in applied chemistry would be approachable if techniques were established to isolate and harvest individual compounds from complex mixtures. For instance, the many unknown but detected compounds in human tissues and environmental samples [1,2] could be subjected to NMR analysis to reveal their structural identity and subsequent bioassay testing to reveal any toxicity. The field of compound-specific isotope analysis (CSIA) is rapidly growing since it can provide information about the source of individual compounds [3,4] and the (kinetic isotope fractionating) processes that chemicals may undergo in the environment [5,6]. 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) [7] which has only recently become commercially available. Initial studies have demonstrated that this technique has the capacity of harvesting microgram-levels of pure individual compounds from complex mixtures [4,8,9]. Briefly, in pcGC the organic extract containing the compounds

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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 (Fig. 1).

The potential of a pcGC system equipped with a CIS and a PFC 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 (aMS) [8]. The ^{14}C age of the individual compounds was then calculated and compared with the age and the history of the bulk samples. The same pcGC system has recently been used in several other studies [3,4,9–11] including harvesting of individual polycyclic aromatic hydrocarbons (PAHs) from environmental standard reference materials followed by successful measurement of their compound-specific ^{14}C abundance [9,12].

Primarily one single research group has now systematically used the pcGC system for the isolation of individual compounds. However, the harvesting efficiency as a function of compound properties and an optimizing scheme of the pcGC-specific operating parameters has never been thoroughly reported. Eglinton et al. [8] investigated the possible sources of contamination of the samples and the potential for isotopic fractionation as a result of the isolation procedure. These workers also investigated the reproducibility of retention times and the purity of harvested material but less detail was provided on the recovery and the effect of varying CIS and PFC operating parameters. In their paper, it was briefly stated that the trapping efficiency will be higher than 80% for PAHs with boiling points below 320 °C [8]. On the other hand, Reddy et al. [12] recently reported that more than 25% of PAHs are lost during the application of pcGC. The objective of the present study was to optimize several instrumental parameters of the pcGC system and to achieve the optimal trapping efficiency of individual PAHs.

The PAHs have been selected as target compounds because of the interest in elucidating the sources of these carcinogenic chemicals to the urban atmos-

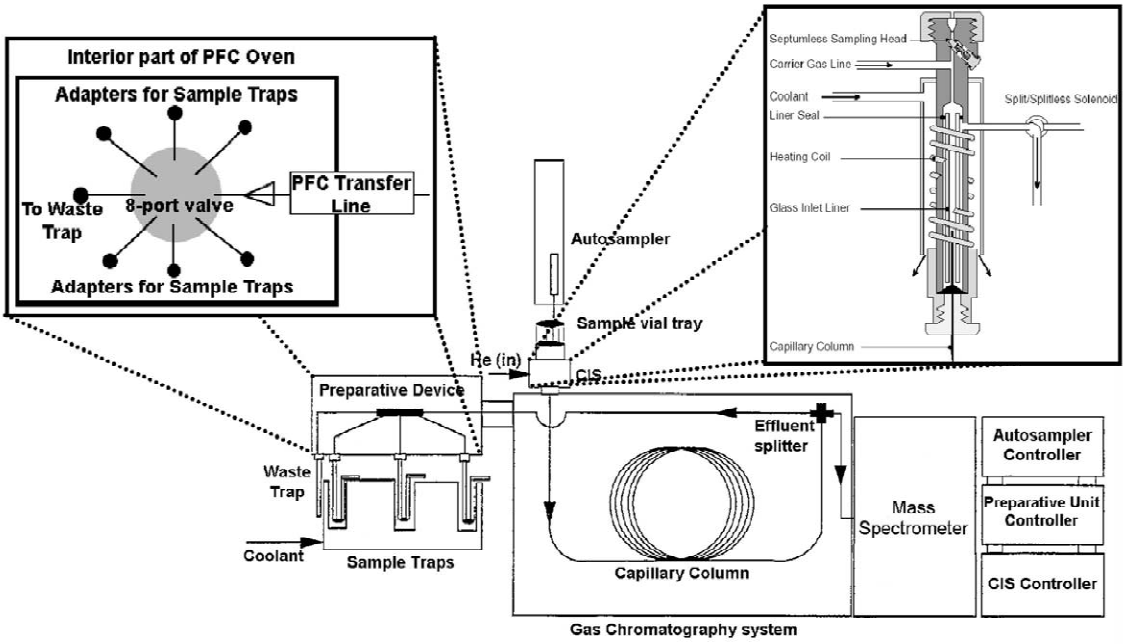

Fig. 1. Automated preparative capillary gas chromatography system used for isolating the PAH peaks [8]. The critical parts of the system (cooled injection system and preparative fraction collector) are also enlarged.

phere 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) [12]. 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 aMS.

2. Experimental

2.1. Materials

All the optimization experiments of the CIS operating parameters were performed using a standard reference material (SRM 2260) prepared by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). This standard reference material is a solution of 24 polycyclic aromatic hydrocarbons (naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, acenaphthylene, acenaphthene, 2,3,5-trimethylnaphthalene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]-fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene) in toluene with a nominal concentration of 60 ng/μl each. The solvent of the SRM 2260 was changed from toluene to hexane before the beginning of the experiments.

Six PAHs (fluorene, retene, chrysene, pyrene, fluoranthene, perylene) were purchased from Sigma–Aldrich (Steinheim, Germany) as pure solids and a solution mixture of these compounds was also prepared in hexane. The concentration of each compound approached 50 ng/μl. This solution was used for the optimization of the PFC switch temperature, PFC trapping temperature and the investigation of the overall performance of the pcGC system after optimization.

2.2. Preparative capillary gas chromatography–mass spectrometry system

The pcGC system used is shown in Fig. 1. The system consists of a Hewlett-Packard (HP) 8590 Series II gas chromatograph, equipped with a mass spectrometer (Hewlett-Packard MSD 5971A) and a HP 7673 Autoinjector, integrated with a Gerstel CIS, a zero-dead volume effluent splitter, and a Gerstel preparative trapping device.

The CIS is claimed to be the most universal injection system available since it eliminates both thermal degradation and chromatographic discrimination [13]. Moreover, this inlet is able to eliminate the coinjected solvent and thus it is compatible with large volume injections, while at the same time greatly improving the chromatography. However, there are several operating parameters that must be properly adjusted to evaporate and vent the solvent via the split line while keeping the target components trapped in the liner before being transferred to the capillary column by thermal desorption. A schematic drawing of a Gerstel CIS inlet is given in Fig. 1. In the CIS inlet, the carrier gas is connected through a septumless sampling head and enters the liner at the top, while a split/splitless valve is attached at the exit. The primary difference between conventional split/splitless inlets and CIS inlets is temperature control. The liner of the CIS can be heated or cooled rapidly. Heating is accomplished using a special heating wire coiled around the liner. A heating rate between 0.5 and 12 °C/s can be selected for this injector. Also, rapid cooling can be performed using a Peltier element.

The preparative device consists of an eight-port zero-dead volume valve in a heated interface and seven 200-μl glass U-tube traps (six sample traps and one waste trap) which are immersed in a coolant. The autoinjector, the CIS and the trapping device are programmable and microprocessor-controlled and MS data are acquired using MS ChemStation software. For time-efficient optimization of the CIS operating parameters, compound separations are achieved using a Supelco SPB-5 (95% dimethyl–5% phenylpolysiloxane) ‘‘megabore’’ (30 m×0.53 mm, 0.5 μm) fused-silica capillary column. Instead, a 60-m capillary column was used during the optimization of PFC switch temperature, PFC trapping

temperature and the investigation of final recoveries of PAHs. A 2-m deactivated capillary tube (0.1 mm I.D.) was used for connecting the splitter effluent with the mass spectrometer while a 0.87-m (0.32 mm I.D.) tube was used for interfacing the effluent splitter with the PFC device.

All the samples were run in hexane as solvent since this was the solvent also selected in previous pcGC studies [10–12]. The injection volume was 5 μl per injection. For the 30-m capillary column, the GC oven temperature was programmed from 40 °C (hold time: 2.08 min) to 170 °C at a rate of 70 °C/min and to 295 °C at a rate of 2.5 °C/min (hold time: 4 min). When the 60-m was used the GC oven temperature was programmed from 40 °C (hold time: 2.08 min) to 170 °C at a rate of 60 °C/min and to 300 °C at a rate of 4 °C/min (hold time: 26 min). The temperatures of the MS detector and the MS transfer line were kept constant through all injections at 290 °C. Helium was used as carrier gas with a constant head pressure of 4 or 9 p.s.i. for the 30-m or the 60-m column, respectively (1 p.s.i=6894.76 Pa). The vent flow was adjusted at 50 ml/min. The CIS inlet was set at 40 °C for 0.08 min (see Section 3.1.1 for optimum solvent venting time) and temperature programmed to 280 °C at a rate of 12 °C/s (hold time: 5 min) and to 150 °C at a rate of 1 °C/s (hold time: 5 min).

In order to determine the portion of the PAHs that reach the mass spectrometer, the split ratio of the effluent splitter had to be specified. Thus, the flow at the exit of the PFC was measured before (6.5 ml/min) and after (5.9 ml/min) the disconnection of the capillary column which links the splitter with the mass spectrometer. It was estimated that about 9% of the total amount that is injected into the CIS will be diverted to the mass spectrometer when a 60-m ''megabore'' column is used. The recoveries obtained in this study (see Sections 3.2.1, 3.2.2 and 3.3) were always corrected against the amount of the PAHs directed to the mass spectrometer detector.

During recovery tests and optimization of PFC switch temperature, the U-tubes containing the trapped compounds were rinsed five times with 250 μl of CH_2Cl_2 and transferred to 2-ml glass vials. CH_2Cl_2 was deliberately selected because it is the ideal solvent when ^{14}C is going to be measured. Its high volatility and the low content of carbon minimize the risk of contamination by ^{14}C-free carbon during the subsequent conversion of trapped samples to graphite targets. All the CH_2Cl_2 extracts were dried to almost dryness and a certain amount of polychlorinated biphenyl (PCB) 153 (Ehrenstorfer, Augsburg, Germany) was added into each sample as an internal standard. The analytes of the final extracts were subsequently quantified by conventional gas chromatography–mass spectrometry analysis.

2.3. Optimization of pcGC parameters

To optimize the pcGC performance, the following six instrumental parameters were investigated in series: CIS solvent venting time, CIS ''stop flow'' mode, CIS splitless time, CIS injection rate, PFC switch temperature and PFC trapping temperature. A series of injections of the SRM solution were made and the signal intensity of each PAH was investigated 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. For the optimization of PFC switch temperature and PFC trapping temperature, six PAHs were trapped under different temperatures at PFC switch and glass traps.

3. Results and discussion

3.1. Optimization of cooled injection system

3.1.1. Solvent venting time

During pcGC harvesting of different compounds, large sample volumes are normally injected into the CIS. The elimination of solvent prior to transferring the sample to the GC column is crucial for the proper operation of the gas chromatography system. The initial conditions of the CIS should be chosen such that the components are retained in the liner by cold trapping, while the solvent is eliminated through the split line. A temperature of 30 °C below the boiling point of the solvent has been suggested by the manufacturer [13] for the solvent venting period. For this reason, a temperature of 40 °C was chosen for these experiments (b.p. of *n*-hexane is 69 °C). Besides inlet temperature, the solvent venting time

should significantly affect the performance of the CIS. This period should be sufficiently long to allow almost all the solvent to evaporate. On the other hand, if the venting time is too long then excessive loss of the target analytes, especially the more volatile, may occur.

Preliminary experiments showed that the injected solvent (5 μl of *n*-hexane) can be removed in about 5 or 10 s when the inlet temperature is 40 °C. Consequently, a series of injections of the SRM solution were made and the signal intensity of each PAH was monitored while the solvent venting time was gradually increased injection by injection from 5 to 120 s. The peak areas of PAHs measured from each injection were normalized against the maximum peak area observed during the corresponding series of injections. PAHs that had molecular mass (M_r) of the same range and thus similar volatility provided similar behavior during variation of solvent venting time. In order to simplify the presentation of the data, PAHs that presented similar variation were grouped together (Fig. 2). An increase of solvent venting time caused a sharp decrease of the signal of the more volatile PAHs (M_r between 128 and 154). The decreased signal intensity of these PAHs to 10%, for solvent venting time higher than 10 s, indicated that these compounds are vulnerable to significant volatilization losses. A less steep decrease was observed for PAHs of intermediate volatility (M_r between 170 and 178). However, the signal of these PAHs decreased by 50% for solvent venting time of ~20 s. In contrast, the less volatile PAHs (M_r between 192 and 276) did not exhibit a significant decrease even for solvent venting time of 2 min. It is obvious that the adjustment of this parameter should be based on the more volatile PAHs. Therefore, solvent venting time should be set at 5 s when PAHs are going to be harvested with pcGC systems equipped with a CIS injector.

3.1.2. Solvent venting in ''stop flow'' mode

A unique feature of the CIS is that solvent venting can also be achieved in a ''stop-flow'' (SF) mode. This feature allows solvent venting to take place while the column head pressure is close to ambient pressure, which further reduces the amount of solvent that can enter the column. Three injections of the SRM solution were repeated for both normal flow (F) mode and for SF mode. The optimal value for solvent venting time (5 s) was used in both cases. In most cases the SF/F ratio was not statistically different than unity indicating that the volatilization losses of the PAHs are not significantly affected by the ''stop flow'' feature (Fig. 3). Only three of the more volatile PAHs (naphthalene, 2-methylnaphthalene and 1-methylnaphthalene) provided ratios between 0.54 and 0.87, which were statistically lower than unity. This may indicate that volatilization

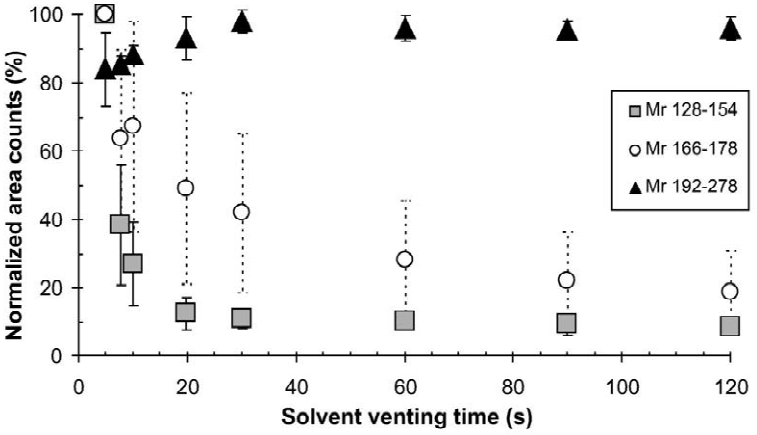

Fig. 2. Relative area counts for three molecular-mass categories of a total of 24 PAHs as a function of solvent venting time. The area counts measured for each category were normalized against the maximum value observed during the corresponding injection series (at $t = 5$ s). The error bars correspond to ±1 standard deviation ($n = 3$).

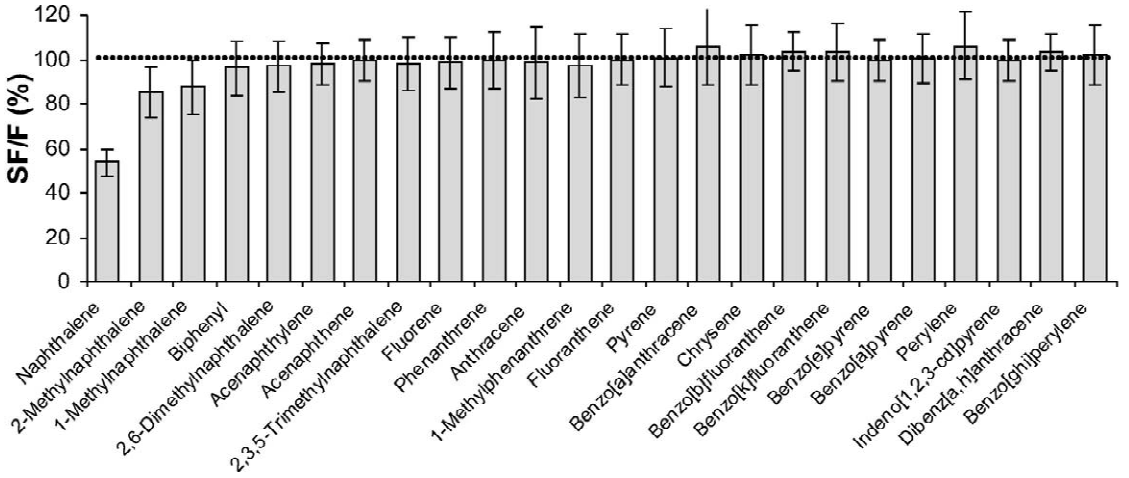

Fig. 3. Ratio of area counts observed when the ''stop flow'' (SF) feature was enabled, divided by the corresponding area counts measured when the column flow was not stopped (F). The error bars correspond to ± 1 standard deviation ($n = 3$).

losses of the more volatile PAHs should be even more intensive during solvent venting when the ''stop flow'' mode is activated. The stop flow should be deactivated during the harvesting of PAHs and especially when the more volatile congeners are under investigation.

3.1.3. Injection rate

The injection rate is known to significantly affect the chromatography when the sample is introduced by hot split or splitless techniques. Low injection rate normally leads to a chromatographical ''discrimination'' and results in a decrease of the relative peak areas of the less volatile compounds. It has been proposed that by introducing the sample at a low initial inlet temperature, many of the disadvantages of the classical hot injection techniques could be circumvented [13] since the sample will be introduced in the liquid phase. Since the HP 7673 Autoinjector is able to inject the samples in fast and slow rate, the effect of the injection rate on PAH recovery was investigated. Three injections of the SRM solution were repeated for both fast and slow mode. The area counts observed for PAH injected in slow mode (SI) were divided by the corresponding area counts measured when the injection was performed in fast mode (FI). In general, SI/FI ratio exhibited a decreasing trend from more volatile to less volatile PAHs (Fig. 4). Only the more volatile PAHs, from naphthalene to acenaphthene provided ratios that were not statistically different than unity, indicating that the injection rate did not significantly affect their signal. However, the SI/FI ratio decreased by almost 50% from acenaphthene to fluoranthene and the ratio of PAHs heavier than fluoranthene approached a constant value of 0.53. It is obvious that a lower injection rate causes a significant discrimination even when the PAHs are injected in a cold CIS inlet (40 °C). Therefore, the maximum injection speed should be selected during harvesting of PAHs by a pcGC system equipped with a CIS.

3.1.4. Splitless time

A very important operation parameter of the CIS is the splitless time. After the solvent venting process, the split vent is closed, the inlet is heated and the compounds are transferred to the GC column. The splitless time corresponds to the time period when the split vent is closed. If the splitless time is too short, significant loss of sample can occur and this could also lead to poor reproducibility. If the splitless time is too long, traces of the solvent can give rise to severe solvent peak tailing. Optimization of this parameter took place by injecting the SRM solution three times each at different splitless times. Again, PAHs of similar molecular mass presented similar variation during the investigation of splitless

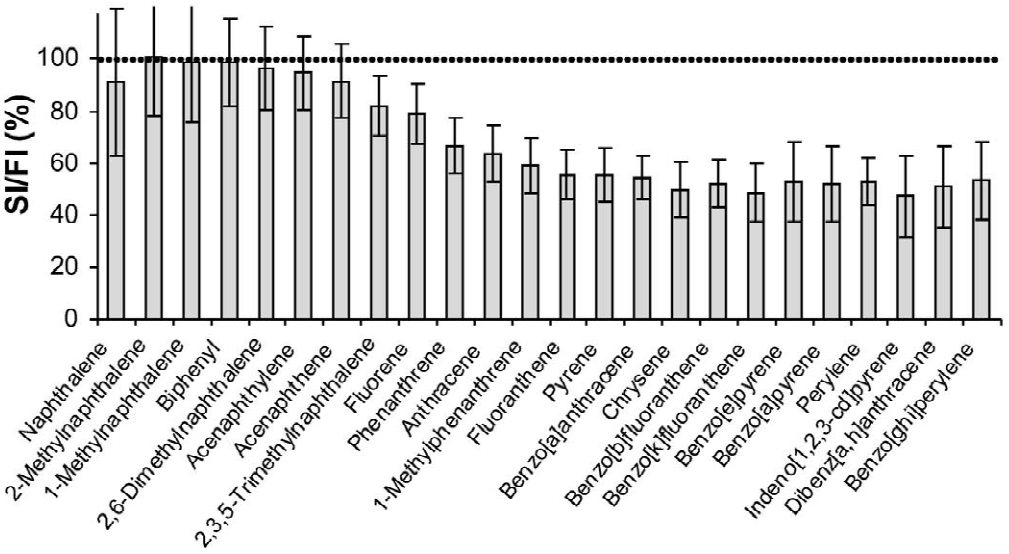

Fig. 4. Ratio of area counts observed when the sample was injected in slow mode (SI), to the corresponding area counts measured when the injection was performed in fast mode (FI). The error bars correspond to ±1 standard deviation ($n=3$).

time and thus they were grouped together for illustrative brevity (Fig. 5).

Volatile PAHs and PAHs of intermediate volatility provided a quite stable signal during the variation of splitless time between 20 and 150 s. Although, the peak areas of these compounds exhibited a slight increase at 20 s, this increase was not statistically significant. Thus, the splitless time could be set in any value between 20 and 150 s without having any substantial effect on the PAHs with molecular masses ranging between 128 and 202.

However, splitless time significantly affected the less volatile PAHs (M_r between 228 and 278). The peak areas of these compounds were sharply decreased to 20% when the splitless time was set lower than 30 s, while no significant change was observed

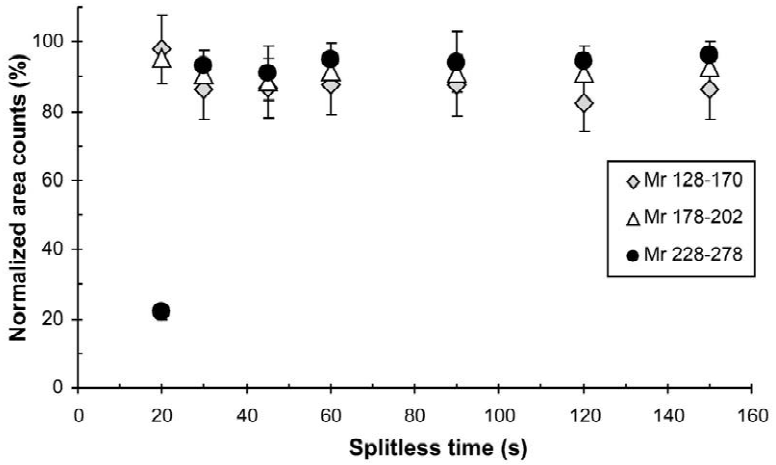

Fig. 5. Normalized area counts for three molecular-mass categories of a total of 24 PAHs as a function of splitless time. The area counts measured for each category were normalized against the maximum value observed during the corresponding injection series. The error bars correspond to ±1 standard deviation ($n=3$).

for higher values. It is obvious that PAHs having higher molecular mass possess a higher boiling point and thus more time should be needed to efficiently volatilize and transfer these compounds from the heated inlet to the entrance of the GC column. In contrast to solvent venting time, the adjustment of splitless time should be based on the less volatile PAHs. Based on the above results, a splitless time of 60 s was chosen for this study.

3.1.5. Reproducibility in retention times and peak areas of PAHs

After the optimization of the CIS inlet parameters, a series of 12 replicate runs were performed on the pcGC system. In general, the retention times did not shift more than a few seconds during the whole series of injections (Table 1). The standard deviation in retention times ranged between 0.01 and 0.03 min (~2 s) with the highest value observed for perylene, which is the last eluting compound in the SRM mixture during gas chromatography (Table 1). The reproducibility of the retention times has previously been investigated in a similar pcGC system and the retention times of *n*-alkanes were reported to exhibit a standard deviation between 0.017 and 0.032 min [8]. These values are thus in agreement with those observed in the present study for PAHs. The reproducibility in the retention times is of great value for the pcGC harvesting of PAHs since the trapping times can be defined within narrow tolerance (e.g. 4 s).

A high reproducibility was also observed for the signal intensity of the PAHs, indicating the excellent performance of the CIS inlet. In general, the relative standard deviation of peak areas approached 8% (Table 1).

3.2. Preparative fraction collector

3.2.1. Optimization of PFC switch temperature

To avoid any condensation of the compounds eluted from the effluent splitter, a heated transfer line is used to interface the GC with the PFC device (Fig. 1). In addition, the eight-port switch and the capillary columns connected with it are located in the PFC oven that can be heated up to 350 °C. The temperature of the PFC oven could be critical when harvesting a series of compounds of significantly varying physico-chemical properties. Low PFC oven temperatures could cause condensation of the less volatile compounds onto the inner surfaces of the PFC switch and capillary columns, while very high temperatures could cause a partial destruction of more temperature-sensitive components.

The effect of the PFC switch temperature during pcGC harvesting of PAHs was investigated with repetitive injections of the solution containing six PAHs at four different switch temperatures between 280 and 340 °C. Afterwards, the trapped compounds of each U-trap were collected and quantified. In order to simplify the presentation of the data, PAHs that presented similar variation were grouped together. The trapping efficiency of fluoranthene, pyrene, retene, and chrysene was quite stable and it

Table 1
Reproducibility of retention times and peak areas for six PAHs from 12 replicate pcGC runs. Average recovery and purity of PAHs after three replicate pcGC recovery experiments are also shown

Compound	Retention time (min)	Peak area (10^7 counts)	Recovery %	Purity %
Fluorene	18.97±0.01	5.4±0.4	47.0±4.7	98.5±0.7
Fluoranthene	31.57±0.01	4.1±0.3	88.3±3.6	99.9±0.1
Pyrene	33.06±0.01	4.3±0.3	89.3±3.9	98.2±2.5
Retene	34.91±0.01	2.6±0.2	91.0±4.3	97.7±1.3
Chrysene	41.91±0.02	3.8±0.3	94.2±5.6	96.6±2.0
Perylene	59.32±0.04	3.5±0.2	102.4±7.2	97.8±1.7

The pcGC system was operated at the optimum conditions. (a) CIS: 5 s CIS solvent venting time, deactivation of CIS ''stop flow'' injection mode, autoinjector ''fast injection'' mode, 60 s CIS splitless time and CIS temperature programming from 40 °C (hold time: 0.08 min) to 280 °C at a rate of 12 °C/s (hold time: 5 min) and to 150 °C at a rate of 1 °C/s (hold time: 5 min); (b) GC: SPB-5 (95% dimethyl–5% phenylpolysiloxane) ''megabore'' (60 m × 0.53 mm, 0.5 μm) fused-silica capillary column and temperature programming from 40 °C (hold time: 2.08 min) to 170 °C at a rate of 60 °C/min and to 300 °C at a rate of 4 °C/min (hold time: 26 min); (c) PFC: 340 °C PFC switch temperature and 30 °C (ambient) PFC trapping temperature.

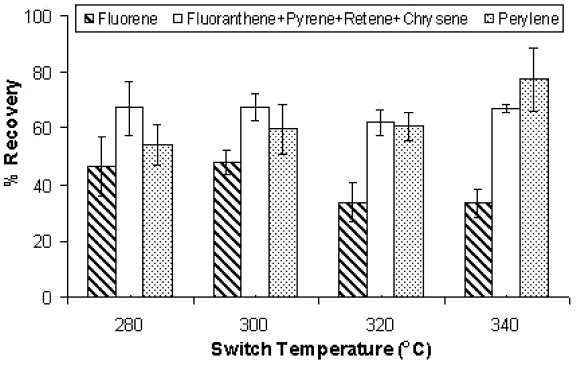

Fig. 6. Trapping recovery of PAHs as a function of switch temperature of the preparative fraction collector (PFC). The temperature of the PFC glass traps was 0 °C (ice-bath). The recoveries have been corrected against the amount of the PAHs directed to the mass spectrometer. The error bars correspond to ±1 standard deviation ($n=3$).

was not dependent on switch temperature (Fig. 6). However, the recovery of fluorene decreased from 47 to 33% when the switch temperature increased from 280 to 340 °C. The partial loss of this compound may be caused by thermal destruction due to the high temperature of the PFC switch. On the other hand, the trapping efficiency of the less volatile perylene exhibited an opposite trend of fluorene, with an increasing recovery from 54 to 77% as the switch temperature increased from 280 to 340 °C (Fig. 6). It is possible that at lower temperatures, a portion of this less volatile PAH condenses onto the capillary transfer columns and/or the PFC switch. Such a condensation might cause a tailing of less volatile PAHs inside the PFC switch and thus a portion of these compounds may be lost at the waste trap. Eglinton et al. [8] mentioned that the trapping recovery efficiency would be higher than 80% for PAHs with boiling points below 320 °C but the efficiency of less volatile PAHs was not commented upon. 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 °C was selected as the optimum value.

3.2.2. Optimization of PFC trapping temperature

In most of the previous studies, the seven glass traps of the PFC device were supported in liquid nitrogen-cooled units to achieve a temperature of −20 °C during the trapping of individual *n*-alkanes [8,11], fatty acids [4,8] or PAHs [9]. More recently, Reddy et al. [12] succeeded in harvesting six PAHs by cryogenically cooling the glass traps at 0 °C. In all cases, it was assumed that cooling at low temperatures should prevent the breakthrough of compounds from glass traps and subsequently higher harvesting recoveries should be achieved.

On the other hand, the manufacturer [14] has suggested that higher temperatures should be applied at the glass traps when PAHs or other semivolatile compounds are going to be harvested. As a rule of thumb the PFC trapping temperature for each analyte should be calculated by Eq. (1):

$$T_{trap} = 0.35(T_{boil} - T_{melt}) \quad (1)$$

where T_{trap} is the ideal PFC trapping temperature (°C) while T_{boil} and T_{melt} are the boiling and the melting point (°C) of the analyte, respectively. According to Eq. (1), the trapping temperature for the PAHs under investigation should range between 62 (fluorene) and 92 °C (fluoranthene).

The effect of the PFC trapping temperature during pcGC harvesting of the six PAH standard analytes was investigated by repetitive injections at three different trapping temperatures (−16, 0 and 30 °C).

The recoveries of PAHs as a function of trapping temperature are presented in Fig. 7. In order to simplify the presentation of the data, PAHs that

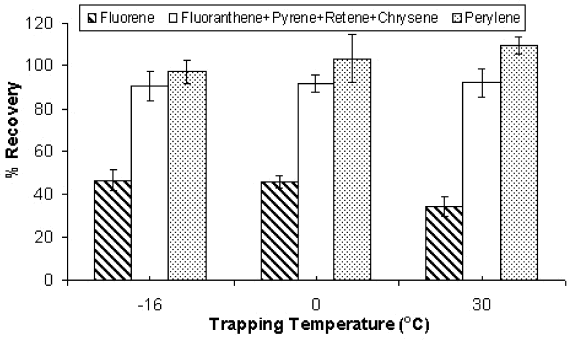

Fig. 7. Trapping recovery of PAHs as a function of trapping temperature of the preparative fraction collector (PFC). The PFC switch temperature was kept constant at 340 °C. The recoveries have been corrected against the amount of the PAHs directed to the mass spectrometer. The error bars correspond to ±1 standard deviation ($n=3$).

provided similar variation were grouped together. In general, high recoveries of 90–100% were obtained for fluoranthene, pyrene, retene and chrysene as well as for perylene at all trapping temperatures (Fig. 7). The exception was fluorene that had recoveries around 50% at −16 and 0 °C and even below 40% at 30 °C. Our results show that the trapping of PAHs is efficient even at ambient (30 °C) temperatures as predicted by Eq. (1). Thus, it is suggested that harvesting of PAHs and other semivolatile organic compounds by pcGC systems should be practically possible even when expensive liquid nitrogen-cooled units are not available.

3.3. Optimized performance of pcGC

The performance of the pcGC system was evaluated for the six individual PAHs at the optimized CIS and PFC operating parameters. During these experiments, the glass traps of the PFC device were supported in ice-bath units and thus the PFC trapping temperature was kept at 0 °C. In addition, each one of the six PAHs was trapped in a separate glass trap. The recovery and the purity of each target analyte were determined after the extraction of the material collected in each glass trap. The average recovery and purity of each analyte after three replicate recovery experiments is shown in Table 1. With the exception of fluorene (50%), the average recoveries for all other PAHs were excellent and ranged between 90% (fluoranthene) and 100% (perylene) (Table 1). Furthermore, the high purity for all PAHs harvested by the pcGC method was achieved. Based on peak areas from conventional GC–MS analysis (total ion chromatograms), the average purity of the PAHs under investigation ranged between 97% (chrysene) and 100% (fluoranthene). The high purity of trapped PAHs confirms the high-performance of the optimized pcGC system. Overall, our results demonstrate that efficient harvesting of individual PAHs can be achieved by using a pcGC system operating at the optimum conditions (5 s CIS solvent venting time, deactivation of CIS ‘‘stop flow’’ injection mode, autoinjector ‘‘fast injection’’ mode, 60 s CIS splitless time, 340 °C PFC switch temperature, and 30 °C (ambient) trapping temperature). 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.

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