Xinyu Zhang[1]
Liang Zhao[1]
Yexin Wang[1]
Yunping Xu[1,2]
Liping Zhou[1,3]

[1]MOE Key Laboratory for Earth Surface Processes, College of Urban & Environmental Sciences, Peking University, Beijing, P. R. China
[2]State Key Joint Laboratory of Environment Simulation and Pollution Control, Peking University, Beijing, P. R. China
[3]Center for Ocean Studies, Peking University, Beijing, P. R. China

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Research Article

Optimization of programmed-temperature vaporization injection preparative capillary GC for compound specific radiocarbon analysis

Preparative capillary GC (PCGC) is a powerful tool for the separation and purification of compounds from any complex matrix, which can be used for compound-specific radiocarbon analysis. However, the effect of PCGC parameters on the trapping efficiency is not well understood. Here, we present a comprehensive study on the optimization of parameters based on 11 reference compounds with different physicochemical properties. Under the optimum conditions, the trapping efficiencies of these 11 compounds (including high-boiling-point *n*-hentriacontane and methyl lignocerate) are about 80% (60–89%). The isolation of target compounds from standard solutions, plant and soil samples demonstrates that our optimized method is applicable for different classes of compounds including *n*-alkanes, fatty acid esters, long-chain fatty alcohol esters, polycyclic aromatic hydrocarbons (PAHs) and steranes. By injecting 25 μL in large volume injection mode, over 100 μg, high purity (>90%) target compounds are harvested within 24 h. The recovery ranges of two real samples are about 70% (59.9–83.8%) and about 83% (77.2–88.5%), respectively. Compared to previous studies, our study makes significant improvement in the recovery of PCGC, which is important for its wide application in biogeochemistry, environmental sciences, and archaeology.

Keywords: Biomarkers / Compound specific radiocarbon analysis / Preparative capillary GC / Programmed-temperature vaporization injection
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1 Introduction

As an important dating method, radiocarbon isotope analysis (^{14}C) has been widely used in geology and archaeology for a long time [1]. This technique also received considerable interest for biogeochemistry and environmental sciences [2–4]. Traditional radiocarbon dating is based on the bulk ^{14}C content of organic or inorganic carbon preserved in sediment, soil, stalagmite, and ice core. However, because of the heterogeneous nature of carbon in those archives, bulk radiocarbon measurement often lacks ability to reveal detailed environmental processes [2, 3, 5]. In contrast, biomarkers are compounds biosynthesized by specific organisms (i.e., vascular plants, algae, bacteria, and archaea) and are capable of distinguishing organic carbon sources at the molecular level [6]. For example, in lake and ocean sediments, long-chain (C_{27}, C_{29}, and C_{31}) and short-chain (C_{15}, C_{17}, and C_{19}) *n*-alkanes are derived from allochthonous terrestrial plants and autochthonous planktons, respectively [6]. Thus, the measurement for isotopic compositions of biomarkers has an advantage in excluding interference from other carbon sources and provides more accurate environmental information.

Preparative capillary GC (PCGC) is a powerful separation tool for carbon and chlorine isotope measurement, structure elucidation, bioactivity assessment, as well as other purposes [2, 7–9]. By applying PCGC, Eglinton et al. first developed a method, compound-specific radiocarbon analysis (CSRA), to collect high purity *n*-alkanes and *n*-fatty acids from oil, plants, and cultural relics and measured their ^{14}C contents by accelerated MS [3]. Subsequent CSRA studies examined ocean and lake sediments [10, 11], aerosols [12, 13], and soils [14]. However, most of biomarkers and pollutants have low concentrations in the environment (ppm or less), while ^{14}C has a natural abundance of only 10^{-12}%. To obtain

Correspondence: Dr. Yunping Xu, MOE Key Laboratory for Earth Surface Processes, College of Urban & Environmental Sciences, Peking University, Beijing 100871, P. R. China
E-mail: yunpingxu@pku.edu.cn
Fax: +86-10-62754411

Abbreviations: Cho, *5a*-cholestane; **CSRA**, compound-specific radiocarbon analysis; **Flu**, fluorene; **Hen**, *n*-hentriacontane; **Hep**, *n*-heptadecane; **Lig**, methyl lignocerate; **Myr**, methyl myristate; **Oct**, octadecyl acetate; **PAHs**, polycyclic aromatic hydrocarbons; **PCGC**, preparative capillary GC; **PFC**, preparative fraction collector; **PTV**, programmed-temperature vaporization; **Squ**, squalane

sufficient amounts of target compounds for ^{14}C measurement (>25 μg carbon), several hundred grams to 1 kg samples are needed [2, 5]. Such a large amount of samples is often not available. This problem can be circumvented by either improving the recovery of PCGC, or lowering the detection limit of accelerated MS, or choosing relatively high abundance compounds (i.e., lignin phenols) as target compounds.

Although several studies used PCGC for CSRA [5,15–17], their efforts focused on the avoidance of contamination rather than the improvement of trapping efficiency. The reported PCGC recoveries range from 40 to 78% with an average of about 50% for various lipid classes (i.e., sterols, fatty acids, *n*-alkanes, *n*-alcohols, and PAHs) [10, 18, 19], although one group achieved exceptionally high recoveries for PAHs (90–100%) [20]. In addition, previous studies usually examined only one class of compounds (i.e., PAHs or *n*-alkanes) [13,20], so, their optimized methods may not be applicable for other classes of compounds.

In this work, we chose 11 reference compounds including *n*-alkanes, *n*-fatty acid esters, sterane, branched chain alkanes, and PAHs to evaluate the effect of PCGC parameters on the trapping efficiencies. Our main objectives are to optimize the parameters of the PCGC system for different types of compounds and improve recoveries and time efficiency to harvest the required amount of carbon (>25 μg) for radiocarbon analysis.

2 Materials and methods

2.1 Chemicals and instruments

All organic solvents used in this study are of Pesticide Grade (Dikma Company, China). Eleven standard chemicals (including three *n*-hydrocarbons, three esters, three PAHs, squalane (Squ), and 5a-cholestane (Cho); Table 1) have purity higher than 95% (J&K Chemicals, Beijing). The reasons for choosing these compounds are that they are important environmental compounds [6] and have a wide range of physicochemical properties. Their molecular weights, boiling points, vapor pressures, and $\log K_{ow}$ range from 166.2 to 436.8 Da, 295 to 458°C, 4.32×10^{-1} to 3.00×10^{-5} Pa at 25°C, and 4.02 to 15.57, respectively (Table 1). These standard chemicals are used for preparation of 11 stock solutions in hexane (5000 μg/mL). The stock solutions are mixed and diluted in dichloromethane (DCM) for preparation of working solution 1 (20 μg/mL) and working solution 2 (100 μg/mL). In addition, two environmental samples, *Fructus Forsythiae* leaves and surface soil, are collected from the Peking University campus and the Saihanba Forest Park (Hebei Province, China), respectively.

An Agilent 7890A GC equipped with an HP 7673A autosampler and a flame ionization detector (FID) is used for quantification of analytes. The separation is achieved on a J&W HP-5 (30 m × 0.32 mm id × 0.25 μm). A GC–MS is composed of an Agilent 7890A GC and a 5975C quadrupole MS detector (EI source, 70 eV). The separation is achieved on a J&W HP-5 MS column (30 m × 0.25 mm id × 0.25 μm).

PCGC is composed of an Agilent GC 7890A and a Gerstel preparative fraction collector (PFC). These two components are connected by a 0.87-m-long deactivate capillary (0.32 μm id). The Agilent 7890A GC is equipped with an FID and programmed-temperature vaporization (PTV) injector (Gerstel, Germany). The separation is achieved on an Agilent DB-XLB (30 m × 0.53 mm id × 1.5 μm). About 1 % of the effluent is diverted to the FID and the remaining 99% are passed. The PFC consists of an oven and seven glass tubes for trapping target compounds. Inside the PFC oven, an eight-port zero-dead volume valve is connected to one transfer line from GC and seven distribution lines (one for waste trap, six for sample traps). The PFC is controlled by a Gerstel modular analytical systems using Maestro software. A 50 μL syringe (Hamilton Company) is used for sample injection. The target compounds are trapped in 100 μL glass tubes by PCGC and rinsed with 500 μL DCM (3×) into two 2 mL glass vials. The solvent is removed under a N_2 stream at 40°C, and the residue is redissolved in 500 μL DCM for analyses.

The hydrogen (purity > 99.999%) used for GC-FID and PCGC is supplied by an HG-1805 hydrogen generator (Kepusheng, Beijing, China). The compressed air is supplied by an AG-1602 air compressor (Kepusheng, Beijing, China). The carrier gas for GC is high purity helium (>99.999%; Hepu Gas, Beijing, China).

2.2 Biomarker extractions

After addition of 20 μg Squ as an internal standard, about 3.4 g dried and pulverized *Fructus Forsythiae* leaves are ultrasonically extracted with 20 mL DCM for 15 min (7×). The combined extracts are rotary-evaporated to dryness and dissolved in hexane by ultrasonication. The fraction containing aliphatic hydrocarbons is obtained by a silica gel column with 10 mL hexane, which is concentrated under a mild nitrogen stream and transferred to a 2 mL glass vial.

For soil, about 80 g freeze-dried sample is ultrasonically extracted by DCM for 15 min (3×). The combined extracts are centrifuged at 3500 rpm for 10 min. The supernatants are rotary-evaporated to 5 mL. The concentrated extract is mixed with 20 mL 1.0 mol/L KOH dissolved in water/methanol (5/95, v/v) and heated at 70°C for 1 h. The extract is rotary-evaporated to remove methanol, after which 20 mL distilled water (DI) is added. After removal of the neutral fraction by liquid–liquid extraction with 25 mL DCM (3×), the remaining fraction is acidified to pH 1 by 6 mol/L HCl and then is subject to liquid–liquid extraction with 25 mL DCM (3×) to obtain fatty acids. The acid fraction is completed dried by rotary evaporation and derivatized with 5 mL 14% BF_3/methanol at 70°C (2 h). The reaction solution containing fatty acid methyl esters (FAMEs) is mixed with 10 mL DI water and extracted with 20 mL hexane (3×). The combined extracts are rotary-evaporated to dry and dissolved with 500 μL DCM in a 2 mL glass vial.

Table 1. Physicochemical properties of 11 reference compounds[a)]

Chemical class	Compounds	Formula	MW	BP[c)] (°C)	logK_{ow}	VP[e)] (Pa at 25°C)
n-Hydrocarbons	Hep[b)]	$C_{17}H_{36}$	240.5	302	8.69	4.32×10^{-1}
	Tri	$C_{23}H_{48}$	324.6	380	11.64	4.72×10^{-3}
	Hen	$C_{31}H_{64}$	436.8	458	15.57	4.55×10^{-5}
PAHs	Flu	$C_{13}H_{10}$	166.2	295	4.02	4.40×10^{-2}
	Flt	$C_{16}H_{10}$	202.3	384	4.93	4.17×10^{-4}
	Pyr	$C_{16}H_{10}$	202.3	404	4.88	4.59×10^{-5}
Esters	Myr	$C_{15}H_{30}O_2$	242.4	323	6.27	3.39×10^{-1}
	Oct	$C_{20}H_{40}O_2$	312.5	NA[d)]	8.72	8.09×10^{-3}
	Lig	$C_{25}H_{50}O_2$	382.6	420	11.18	3.00×10^{-5}
Other hydrocarbon	Squ	$C_{30}H_{62}$	422.8	350	14.63	3.67×10^{-2}
	Cho	$C_{27}H_{48}$	372.7	441	10.36	1.17×10^{-5}

a) Data are from the ChemSpider database (http://www.chemspider.com).
b) Hep, *n*-heptadecane; Tri, *n*-tricosane; Hen, *n*-hentriacontane; Flu, fluorene; Flt, fluoranthene; Pyr, pyrene; Myr, methyl myristate; Lig, methyl lignocerate; Oct, octadecyl acetate; Squ, squalane; Cho, *5a*-cholestane.
c) BP: boiling point.
d) NA: not available.
e) VP: vapor presure.

2.3 GC oven programs

For mixed standards, the GC oven is programmed from 60°C (hold time: 5.9 min) to 190°C at a rate of 25°C/min, and then increased to 200°C at a rate of 2°C/min (hold time: 3 min). After that, the oven temperature is further heated to 250°C at a rate of 20°C/min (hold time: 1 min), and finally ramped to 300°C at a rate of 25°C/min (hold time: 13 min).

For *n*-alkanes from plant leaves, the GC oven is programmed from 60°C (hold time: 5.9 min) to 270°C at a rate of 25°C/min, and further increased to 300°C at a rate of 5°C/min (hold time: 17 min).

For FAMEs from forest soils, the GC oven is programmed from 60°C (hold time: 5.9 min) to 310°C at a rate of 6°C/min, isothermal at 310°C for 25 min.

2.4 Quantification of analytes

The injection efficiency is calculated according to relative peak areas of analytes on PCGC under different conditions where maximum peak areas are assumed as 100%. The recovery of analytes is calculated according to peak areas of GC-FID before and after trapping on PCGC, which is expressed as the following equation:

$$\text{Recevery} = \frac{\text{Amount collected}}{\text{Amount injected}} \times 100\% = \frac{A_c \times \left(\frac{V_{0,c}}{V_{c,inj}}\right)}{A_s \times V_{s,inj} \times n} \times 100\%$$

A_c, peak area of the collected compound on GC-FID; $V_{0,c}$, the total volume of original sample; $V_{c,inj.}$, the injection volume for GC-FID; A_s, peak area of the collected compound in original sample on GC-FID; $V_{s,inj.}$, the injection volume for PCGC; n, the repetitive injection times on PCGC. All the peak areas are average values of three injections on GC-FID.

3 Results and discussion

3.1 Orthogonal experiment design

A number of parameters related to PTV injector, such as inlet initial and final temperature, injection speed, vent time, flow and pressure, inlet heating rate, and oven initial temperature, can influence injection efficiency. In order to reduce the number of variables to optimize, a $L_{18}(3^7)$ orthogonal table was used (Supporting Information Table S1). The result (Table S2) showed that the relative importance was vent time > vent flow > inlet initial temperature > injection speed > inlet heating rate, vent pressure, and oven initial temperature. Since inlet heating rate, vent pressure, and oven initial temperature are the least important for the injection efficiency, they are set as 720°C/min, 10 psi, and 60°C, respectively, and are not further optimized. In the following experiments, the PTV inlet parameters to be optimized include inlet initial and final temperature, inlet transfer time (the time between solvent vent finishes and inlet split flow starts), injection speed, vent flow, and vent time.

3.2 Optimization of PTV inlet

3.2.1 Inlet final temperature

Three inlet temperatures (250, 300, and 350°C) were used to evaluate the effect on the injection efficiency. Under the same inlet final temperature, the vapor pressures/boiling points of analytes are the most important factors controlling the

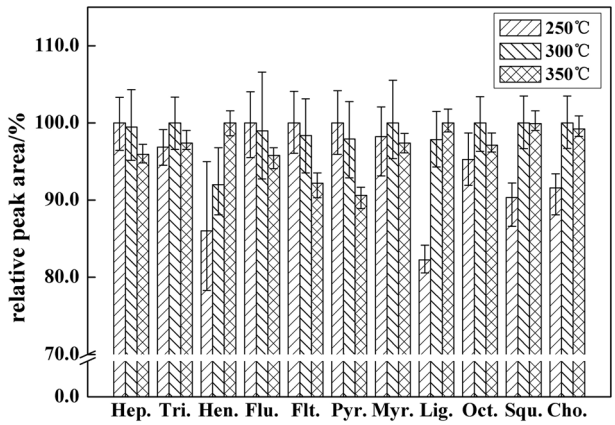

Figure 1. Injection efficiencies under different inlet final temperatures. Other programmed-temperature vaporization (PTV) parameters were set as follows: injection speed (10 000 μL/min), inlet initial temperature (20°C; hold 0.5 min), inlet heating rate (720°C/min), vent flow (20 mL/min), vent pressure (10 psi), vent time (30 s), transfer time (15 min), oven initial temperature (60°C; hold 1 min). The error bars correspond to ±1 SD ($n = 3$).

injection efficiency (Fig. 1). This is no surprise since these two parameters present a strong positive correlation for reference compounds ($r = 0.93$). With the inlet final temperature increasing from 250 to 350°C, the injection efficiencies of low-boiling-point compounds (<380°C) such as methyl myristate (Myr), *n*-heptadecane (Hep), *n*-tricosane (Tri), and octadecyl acetate (Oct) remained relatively constant (±10%), while those of high-boiling-point compounds (>400°C), such as *n*-hentriacontane (Hen), methyl lignocerate (Lig), and Cho increased by 20%. Our result demonstrates that higher inlet final temperature (350 °C) has a positive effect on the injection efficiency of high-boiling-point compounds. However, the injection efficiencies of all three PAHs displayed a slight decreasing trend with increasing inlet final temperature. Thus, a ubiquitous optimum inlet final temperature is not available. Considering that long-chain *n*-alkanes, long-chain fatty acids and steranes are widely used biomarkers [6], we set 350°C as the inlet final temperature for further optimization.

3.2.2 Transfer time

Three repetitive injections showed that injection efficiencies of all reference compounds consistently increased as the transfer time changed from 0 to 4 min (Fig. 2A), suggesting more evaporation of analytes with increasing transfer time. Over 95% of Hep, PAHs, and Myr have been transferred to the GC column when the transfer time reached 4 min. In contrast, the injection efficiencies of high-boiling-point analytes (i.e., Hen, Lig, Squ, and Cho) further increased by 35% when the transfer time increased to 15 min. Such disparity is attributed to the different time required to transfer less and more volatile compounds from the PTV liner to the GC column. In order to quantitatively transfer all compounds to the GC column, we set 15 min as the optimum transfer time.

3.2.3 Injection speed

In this study, the injection speed varied from 100 to 10 000 μL/min. No compounds were detected at the injection speed of 100 μL/min (Fig. 2B), agreeing with the previous report that lower injection rate causes a significant discrimination on the chromatography of analytes [20]. When the injection speed is too slow, the failure in liquid film formation inside the liner will hamper the evaporation of solvent and analytes. With the injection speed increasing to 300 μL/min, most of analytes reached their maximum injection efficiencies (Fig. 2B). Further increase in the injection speed caused a decrease in the injection efficiencies by about 10% for low-boiling-point compounds and 30% for high-boiling-point compounds (Fig. 2B), suggesting an injection speed of >300 μL/min exceeding the solvent elimination rate. Based on these facts, we chose 300 μL/min as the optimum injection speed.

3.2.4 Inlet initial temperature

Although an inlet temperature of 30°C below the boiling point of solvent is recommended for solvent elimination [20], a higher inlet initial temperature is beneficial for transferring less volatile analytes to the GC column. In order to assess the influence of inlet initial temperature on injection efficiency, we increased this temperature from 20 to 100°C by 20°C steps. During this process, the injection efficiencies of low-boiling-point compounds (such as Hep, fluorene (Flu), and Myr) decreased by 45%, while high-boiling-point compounds (such as Hen and Lig) reached their highest injection efficiencies at 80°C (Fig. 2C). This result suggests no ubiquitous optimum inlet initial temperature available for all reference compounds. Since Hen and sterane are thought to be most difficult to trap on the PCGC system [5], we set the inlet initial temperature at 80°C for further optimization.

3.2.5 Vent flow and vent time

When the vent flow increased from 20 to 500 mL/min, the injection efficiencies of more volatile compounds such as Hep, Flu, Myr, and Oct decreased by 80%, while those of less volatile compounds such as Hen, Lig, and 5α-sterane varied in less than 10% (Fig. 2D). This result suggests that volatile compounds are easily loss *via* the split vent under the higher vent flow. Thus, 20 mL/min has been chosen as the optimum vent flow in order to quantitatively transfer all reference compounds from the injector to the GC column.

With the vent time varying from 5 to 100 s, the injection efficiencies of 11 compounds unanimously decreased (Fig. 2E), suggesting that longer vent time will cause substantial loss of target compounds *via* the split vent. Therefore, we choose 5 s as the optimum vent time.

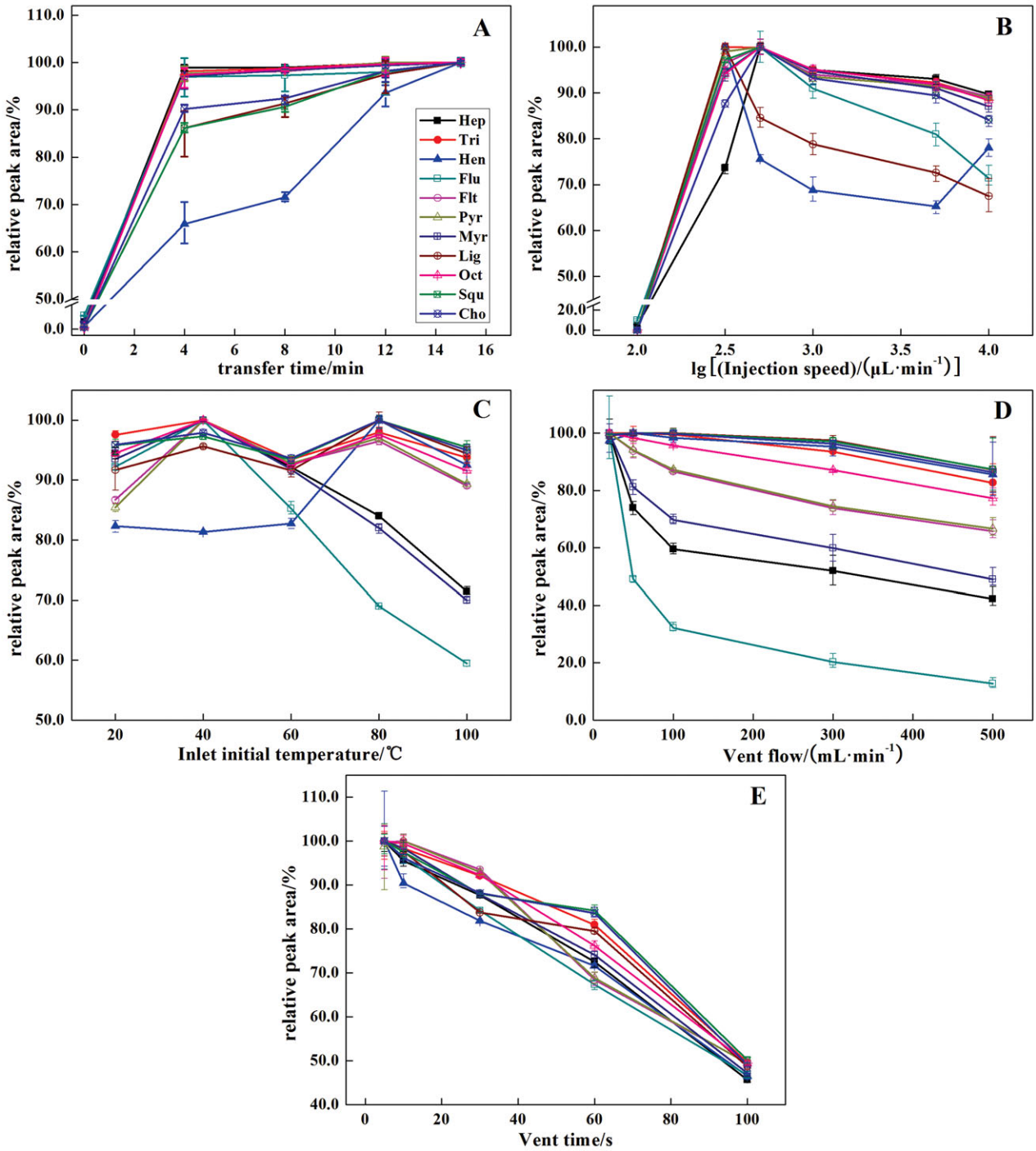

Figure 2. Optimization of the preparative capillary GC (PCGC) parameters related to the programmed-temperature vaporization (PTV) injector: (A) transfer time; (B) injection speed; (C) inlet initial temperature; (D) vent flow; (E) vent time. The default values were: injection speed (10 000 μL/min), inlet initial temperature (20°C; hold 0.5 min), inlet heating rate (720°C/min), inlet final temperature (350°C), vent flow (20 mL/min), vent pressure (10 psi), vent time (30 s), oven initial temperature (60°C; hold 1 min). These values are subject to change after optimization for respective parameters. The error bars correspond to ±1 SD ($n = 3$). The recovery of pyrene is calculated according to the amount of target compound and its chlorination product, monochloropyrene.

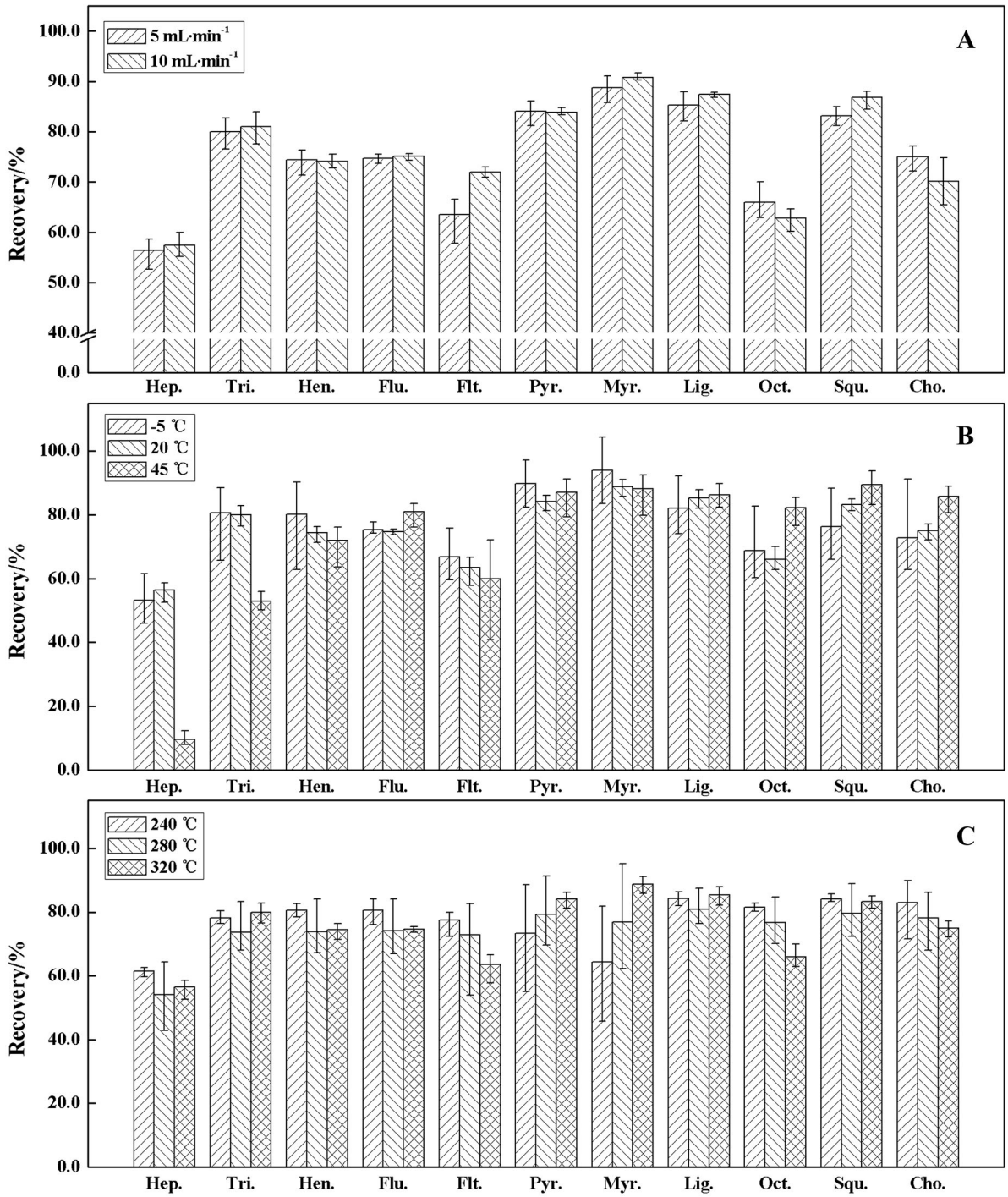

Figure 3. Optimization of the preparative capillary GC (PCGC) parameters related to preparative fraction collector (PFC): (A) carrier gas flow; (B) trapping temperature; (C) transfer line and oven temperature. The parameters related to the programmed-temperature vaporization (PTV) injector were set as optimized conditions (see text). The error bars correspond to ±1 SD ($n = 3$). The recovery of pyrene is calculated according to the amount of target compound and its chlorination product, monochloropyrene.

3.3 Optimization of PFC parameters

After optimizing the parameters of the PTV injector, we continue to assess the effect of the PFC parameters on the trapping recovery. During this process, the conditions of the PTV injector are set as the follows: inlet initial temperature (80°C); inlet final temperature (350°C); inlet heating rate (720°C/min); transfer time (15 min); injection speed (300 μL/min); vent flow (20 mL/min); vent time (5 s); vent pressure (10 psi); oven initial temperature (60°C).

Table 2. PCGC recoveries of compounds from different samples under the optimum conditions

Trap no.	Mixed standard-2		*Fructus Forsythiae* leaves				*Mongolica Litv* forest soil			
	Compounds	Recovery (%)	Compound name	Amount[a] (μg)	Recovery (%)	Purity (%)	Compound name	Amount (μg)	Recovery (%)	Purity (%)
1	Flu	73.8	*n*-C_{25}	6.6	81.1	86.7	*n*-C_{14} FA[b]	18.1	88.5	93.5
	Hep	81.5								
	Methyl myristate	80.9								
2	Fluoranthene	81.5	Squ	3.2	83.8	85.3	*n*-C_{20} FA	83.1	83.1	98.8
	Pyrene	78.7								
	Oct	79.2								
	n-Tricosane	82.2								
3	Squ	69.3	*n*-C_{27}	33.2	79.1	99.0	*n*-C_{24} FA	93.5	87.8	100.0
4	Lig	78.4	*n*-C_{29}	72.0	59.9	100.0	*n*-C_{26} FA	37.5	84.2	100.0
5	Cho	80.8	*n*-C_{31}	143.6	77.2	99.5	*n*-C_{28} FA	30.3	83.8	96.8
6	Hen	78.0	*n*-C_{33}	9.6	63.2	99.0	*n*-C_{30} FA	26.6	77.2	89.5

a) The amount of trapped compound was determined by the external standard method on GC-FID.
b) FA: fatty acid.

3.3.1 Carrier-gas flow

Due to large different temperature between the PFC oven and the glass traps, the vaporized compound in the PFC oven may rapidly condense at the end of the distribution line. On the other hand, the thermally unstable compounds have potential to degrade in hot transfer and distribution lines. Thus, higher carrier-gas flow is theoretically useful for improving the trapping recoveries of PCGC. However, no significant difference was observed for the trapping efficiencies of 11 reference compounds when the carrier-gas flow increased from 5 to 10 mL/min (Fig. 3A). Thus, 5 mL/min was set as the optimum carrier-gas flow.

3.3.2 Trapping temperature

There are controversies about the optimum trapping temperature in previous studies. Some researchers proposed that low trapping temperature would prevent breakthrough of target compounds and used liquid nitrogen for cooling traps [5], while others thought that the trapping temperature is not an important factor for the recovery and thus used room temperature to trap target compounds [11]. A recent study used relatively high trapping temperature (i.e., 60°C) in order to avoid condensation of high-boiling-point compounds, such as long-chain ($\geq n$-C_{24}) alkanes and FAMEs at the end of distribution lines [21].

Here, we tested the effect of three trapping temperatures (−5, 20, and 45°C) on the PCGC recovery. Our results (Fig. 3B) showed that for low-boiling-point compounds, such as Hep and Flu, the recoveries substantially decreased by 80% when the trapping temperature increased from −5 to 45°C, attributed to great loss of analytes *via* evaporation under relatively high trapping temperature. For high-boiling-point compounds, such as Cho and Lig, the recovery slightly increased by 10% as the trapping temperature increased to 45°C. However, monochloropyrene, a chlorination product of pyrene (Pyr) [22], was identified when trapping temperature was 45°C. Based on these facts, the best trapping temperature was −5°C for low-boiling-point compounds (such as Flu and Hep) and pyrene, and 45°C for high-boiling-point compounds, such as Cho and methyl lignocaine (Lig).

3.3.3 Transfer line and PFC oven temperature

To avoid the condensation of compounds from capillary to sample traps, the transfer line and PFC oven is usually maintained at a temperature higher than the GC oven [5]. However, the transfer line temperature should not be too high since some compounds may degrade and column bleeding may dramatically increase otherwise. Here, we set the transfer line and PFC oven temperature at 240, 280, and 320°C. No clear relationship was observed between recoveries of 11 compounds and transfer line/PFC oven temperature (Fig. 3C). With the temperature varying from 240 to 320°C, the recoveries of Tri and Oct increased by 25%, while those of Lig decreased by 20%. Considering that column bleeding dramatically increases when the temperature is higher than 300°C, we set 280°C as the optimum transfer line and PFC oven temperature.

3.4 Applicability of the optimized method for environmental samples

Three different samples, namely, working solution 2, plant leaves, and forest soil, were used to test our optimized PCGC method. Traditionally, the PCGC injection volume is 3–5 μL [5]. In order to obtain sufficient amounts of target compounds for CSRA, over 100 injections are needed [2]. In

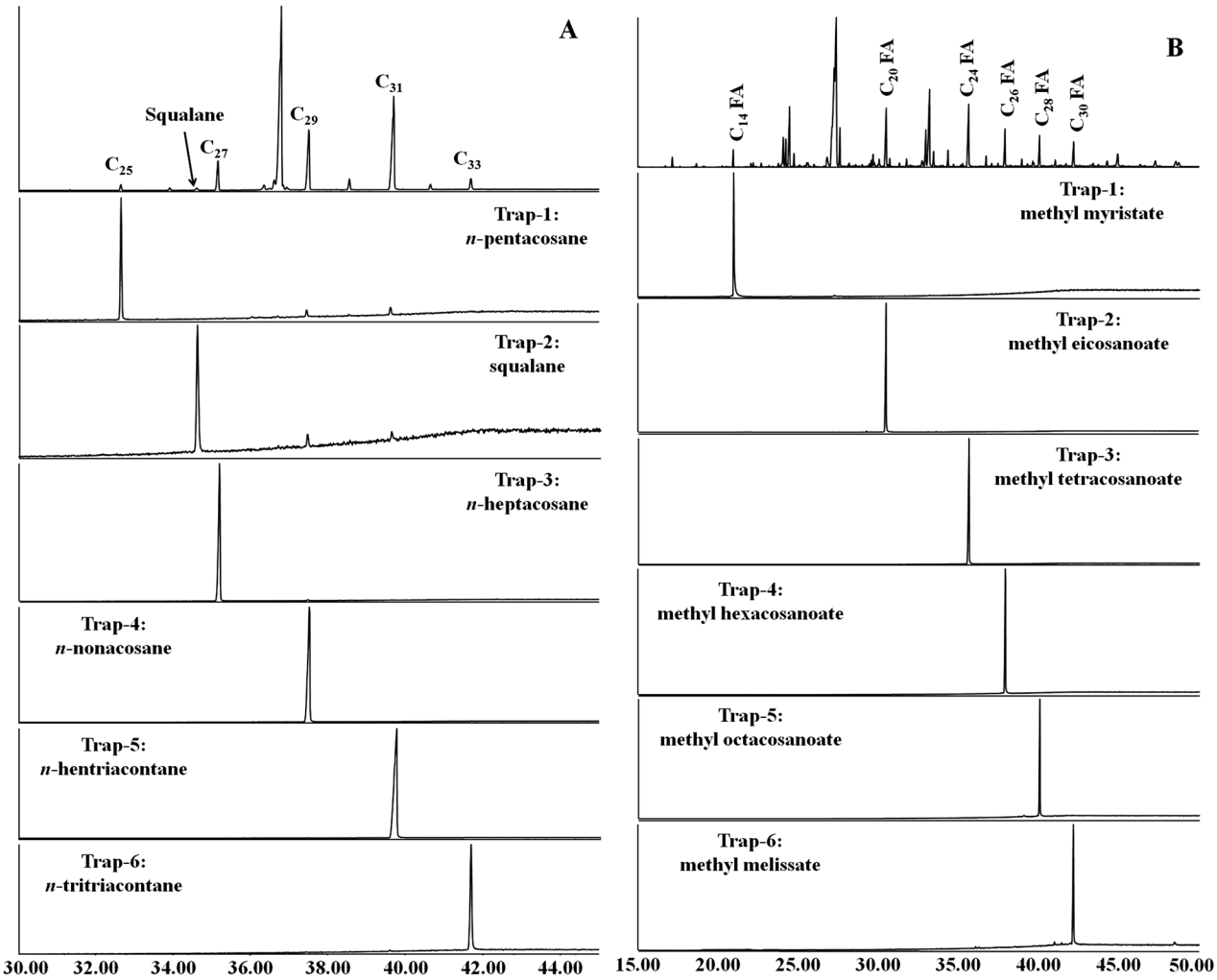

Figure 4. Preparative capillary GC (PCGC) separation of the target compounds from different samples: (A) *n*-Alkanes from plant leaves and (B) fatty acids from forest soil.

this work, we increased the injection volume to 25 μL by applying the PTV inlet solvent vent mode. Under our optimum PCGC conditions, average trapping efficiencies of mixed standard 2, *n*-alkanes (C_{25}–C_{33}), and fatty acid (C_{14}–C_{30}, saturated) methyl esters were 69.3–82.2, 59.9–83.8, and 77.2–88.5%, respectively (Table 2). The purity of target compounds is generally higher than 90% based on GC–MS (Fig. 4), and about 100 μg of single compound can be harvested within 24 h (Table 2). Comparing with 40–50% for average recoveries achieved in previous studies [10, 18, 19], our study has made significant improvements in the trapping efficiency, thus, reducing sample amount required for CSRA.

4 Concluding remarks

We present a comprehensive study on the optimization of PCGC parameters based on 11 reference compounds with different physicochemical properties. The optimum PCGC conditions are inlet final temperature (350°C), inlet heating rate (720°C/min), transfer time (15 min), injection speed (300 μL/min), vent flow (20 mL/min), vent time (5 s), vent pressure (10 psi), carrier gas flow (5 mL/min), PFC oven, and transfer line temperature (280°C). No ubiquitous optimum conditions are available for trapping temperature and inlet initial temperature. The optimum trapping temperature is −5°C for low-boiling-point (<380°C)/thermally unstable compounds and 45°C for high-boiling-point compounds (>400°C), while the optimum inlet initial temperature is 20°C for low-boiling-point compounds and 80°C for high-boiling-point compounds. Under the optimum conditions, the recoveries of 11 reference compounds, *n*-alkanes from plant leaves, and *n*-fatty acids from forest soil range from 59.9 to 88.5% with an average of about 80%. By increasing injection volume to 25 μL, we harvest over 100 μg target compounds within 24 h. Compared to previous studies, this study makes significant improvements in the recovery and time efficiency, which is helpful for wide application of CSRA in geology, archaeology, and environmental sciences.

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The authors have declared no conflict of interest.

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