SEPARATION PERFORMANCE OF PEG-LINKED CALIX[4]ARENE AS STATIONARY PHASE FOR CAPILLARY GAS CHROMATOGRAPHY

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This work presented a new PEG modified calix[4]arene stationary phase (C4A-PEG-2PTSC) for gas chromatographic (GC) separations. The statically coated C4A-PEG-2PTSC column exhibited moderate polarity and column efficiency of 2224 plates m^{-1} determined by 1-octanol at 120 °C. The results showed that the C4A-PEG-2PTSC column exhibited the good separation performance for various types of analytes containing halogenated benzenes, benzaldehydes, phenols, alcohols, anilines isomers and showed the different retention behavior with the comparative columns. Importantly, it showed the better separation capacity of toluidine and xylidine isomers than commercial HP-35 column. Moreover, it was applied in practical sample analysis to detect the content of isomer impurities. This work exhibited the good application potential of C4A-PEG-2PTSC stationary phase in GC analyses.

Keywords: capillary gas chromatography; stationary phase; calixarene; separation performance.

INTRODUCTION

Gas chromatography (GC) is a common separation and analysis technology in petrochemical, environmental monitoring, food analysis, biological medicine and other fields because of its fast analysis speed, high sensitivity and high selectivity.[1-4] The chromatographic stationary phase with high selectivity is a key factor for the efficient separation of analytes in GC. In the recent decades, some new stationary phases have been reported, such as macrocyclic compounds, polymers, ionic liquids, MOFs, COFs, etc.[5-11]

Calixarene is the third-generation supramolecular macrocyclic host compound after crown ethers and cyclodextrins,[12] and it has received extensive attention in the field of analysis due to their unique physicochemical properties such as adjustable cavity size, good structural/thermal stability and so on. According to the previous researches,[13,14] the unsubstituted calixarenes used as GC stationary phase had poor film-forming property on the inner wall of the capillary column, resulting in its bad separation ability for the most analytes. However, calixarenes had multiple active sites and can be modified to improve the separation performance. Śliwka-Kaszyńska *et al*. synthesized five different calix[4]arene stationary phases and investigated their separation capacity and interaction mechanism for the various types of polycyclic aromatic hydrocarbons (PAHs).[15] In addition, our group was devoted to the research on new calixarene stationary phases. We firstly reported the amphiphilic calix[4]arene (C4A-NH$_2$) stationary phase to separate aniline isomers in 2019.[16] Subsequently, we synthesized other calixarene derivatives to as stationary phases and they all showed excellent separation performance.[17,18]

Poly (ethylene glycol) (PEG) is a common polymer, which is composed of multiple repeating units of (CH$_2$CH$_2$O)$_n$, and the hydroxyl groups at the ends of PEG greatly increase the polarity, and allow H-bonding and dipole-dipole interactions with solutes molecules. At present, the applications of PEG have involved many fields like biomedicine, catalysis, energy fuels, and chromatographic separation, etc.[19-22] In the GC, PEG is a common polar stationary phase.

Delmonte *et al*. reported the selectivity of PGE stationary phase for the fat and oil analytes.[23] Shende *et al*. prepared sol-gel PEG stationary phase showing high resolution for carboxylic acids and aliphatic amines.[24] Poole *et al*. reported PEG stationary phases with dipolar nature, strongly hydrogen-bond basic, no hydrogen-bond acidity, and moderate cohesion.[25] It can be seen that PEG stationary phase exhibited outstanding separation performance for the various analytes. Thus, we proposed a new modification strategy for calixarenes as GC stationary phase.

In this work, we designed a new stationary phase namely C4A-PEG-2PTSC which combined 3D π-rich cavity of calix[4]arene with polar chains of PEG. The C4A-PEG-2PTSC stationary phase obtained by this strategy possessed the lower melting point than calixarene, better film-forming ability, higher column efficiency and better separation capacity.[26,27] Its upper rims were four non-polar *p-tert*-butyls, the lower rims were two unsubstituted hydroxyl groups and two polar PEG chains sealed by *p*-toluenesulfonyl chloride, respectively. The amphiphilic structure can improve the selectivity of C4A-PEG-2PTSC for analytes with different polarities. In this paper, the C4A-PEG-2PTSC was investigated by column efficiency, polarity and thermal stability. Then, its selectivity and separation ability were tested by Grob mixture, the mixture of 23 analytes, positional and structural and *cis-/trans-* isomers. Meanwhile, the C4A-C10, commercial HP-35 and PEG-20M columns were used as the references.

EXPERIMENTAL

Materials and Instruments

Calix[4]arene (C4A), PEG (average Mn 2000), triethylamine (TEA) and K$_2$CO$_3$ were purchased from Energy Chemical, *p*-toluenesulfonyl chloride (PTSC) was bought from Sinopharm Chemical Reagent Co., Ltd. Dichloromethane (DCM) and acetonitrile (ACN) were purchased from Damao Chemical Reagent Factory (Tianjin, China).

All the commercial reagents were analytical grade and without further purification, including Grob mixture composed of *n*-decane, *n*-undecane, nonanal, 1-octanol, 2,3-butanediol,

methyl decanoate, methyl undecanoate, methyl dodecanoate, 2,6-dimethylaniline, dicyclohexylamine, 2,6-dimethylphenol and 2-ethylhexanoic acid, and a complex mixture of 23 analytes composed of *n*-decane, ethylbenzene, 1-bromohexane, 2-heptanone, *n*-propylbenzene, 1,3,5-trimethylbenzene, 1-bromoheptane, 2-octanone, 1,2,3-trimethylbenzene, 1-hexanol, *n*-tridecane, 1,4-dichlorobenzene, 1-heptanol, methyl nonanoate, 1-octanol, *n*-pentadecane, 1-nonanol, 1,2,3-trichlorobenzene, *o*-toluidine, 2,6-dimethylaniline, 2,5-dimethylaniline, 4-chloronitrobenzene and 1-dodecanol.

The untreated fused-silica capillary column (0.25 mm, i.d.) was bought from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). The commercial HP-35 capillary column (15 m × 0.25 mm, i.d., 0.25 μm film thickness) was bought from Agilent Technologies Co. Ltd. (Palo Alto, California, USA) and the commercial PEG-20M capillary column (15 m × 0.25 mm, i.d., 0.25 mm film thickness) was bought from Lanzhou Atech Technologies Co. Ltd. (Gansu, China) for comparison.

GC separations were determined on an Agilent 7890A GC system equipped with a split/splitless injector and a flame ionization detector (FID). All the GC separations were performed under the following conditions: nitrogen of high purity (99.999%) as carrier gas, injection port at 300 °C, split injection mode at a split ratio of 100:1 and FID detector at 300 °C, the specific temperature program and flow rate of carrier gas were indicated in the caption of each figure. IR spectrum was recorded on a Tensor II FT-IR spectrometer. ^{1}H NMR spectrum and ^{13}C NMR spectrum were recorded on a Bruker Biospin 400 MHz instrument using TMS as the internal standard. The chemical shifts (δ) were reported in ppm.

Synthesis of the C4A-PEG-2PTSC stationary phase

The synthesis route of C4A-PEG-2PTSC was described in Figure 1.[28,29] Firstly, PEG (6.29 g, 3.15 mmol), *p*-toluenesulfonyl chloride (PTSC) (0.60 g, 3.15 mmol) and TEA (20 mL) were added into DCM (20 mL). The mixture was stirred for 2 h at 25 °C. Then, a small amount of HCl solution was added dropwise to neutralize excess TEA. The mixture was filtered and evaporated in vacuum, the yellow oily liquid (PEG-PTSC) was obtained (4.746 g, 70% yield). IR (KBr, cm^{-1}): 1094.54 (C-O-C), 1176.90 (S=O), 1188.93 (C-O-C), 1454.76 (C=C), 1598.27 (C=C), 2863.16 (CH$_2$). Afterwards, C4A (0.50 g, 0.77 mmol), PEG-PTSC (1.92 g, 0.89 mmol) and K$_2$CO$_3$ (0.96 g, 6.96 mmol) were added into ACN (20 mL) and stirred at 85 °C for 24 h under nitrogen atmosphere. After the reaction, the mixture was washed with deionized water (3 x 15 mL), dried with anhydrous magnesium sulfate and concentrated in vacuum. Thus, a yellow solid crude product was obtained and purified by column chromatography [MeOH/DCM (*v/v* = 1:9)]. Finally, a light yellow solid was obtained (80% yield). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.79 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.1 Hz,

2H), 7.17 - 7.11 (m, 4H), 7.02 (s, 4H), 6.86 - 6.71 (m, 4H), 4.35 (s, 2H), 4.32 (s, 2H), 4.17 - 4.11 (m, 8H), 3.82 - 3.61 (m, H$_a$ + H$_b$), 3.46 (d, *J* = 4.8 Hz, 4H), 2.44 (s, 6H), 1.27 (s, 18H), 1.00 - 0.90 (m, 18H), ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 129.87 (s), 128.02 (s), 126.05 (s), 72.56 (s), 70.60 (s), 61.71 (s), 33.86 (s), 31.79 (s), 31.09 (s); IR (KBr, cm^{-1}): 730.25 (CH$_2$), 1098.02 (C-O-C), 1239.46 (S=O), 1349.27 (C-O), 1455.07 (C=C), 2866.52 (CH$_2$), 3518.25 (OH).

Fabrication of the C4A-PEG-2PTSC capillary column

Using untreated fused silica capillary column (10 m × 0.25 m, i.d.) to prepare the C4A-PEG-2PTSC column. Before static coating, the column was pre-treated with a saturated solution of NaCl-MeOH to rough its inner wall. Then, the saturated solution was removed and the column was raised to 200 °C and maintained 3 h under nitrogen. Then, the stationary phase was dissolved in DCM (0.15%, w/v) and coated on the inner wall of the capillary column by static method.[30] Specifically, sealed one end of the column and the other end was connected to the vacuum system, and the DCM solvent was slowly evaporated at a constant temperature of 40 °C. Finally, the C4A-PEG-2PTSC column was conditioned from 40 °C (keep 30 min) to 160 °C for 7 h at the rate of 1 °C min^{-1} under nitrogen.

RESULTS AND DISCUSSION

Characterization of the C4A-PEG-2PTSC column

The inherent thermal stability of the C4A-PEG-2PTSC was determined by thermal gravimetric analysis (TGA). As shown in Figure 2(a), C4A-PEG-2PTSC presented about 5% mass loss at 238 °C. Compared with the TGA of PEG (191 °C, 5% mass loss), it had a distinct improvement, suggesting that the C4A-PEG-2PTSC can be applied for GC separations. As can be seen in the Figure 2(b), the Golay curve was plotted by the heights equivalent to a theoretical plate (HETP) with different flow rates at 120 °C, and it displayed the minimum HETP of 0.45 mm at 12 cm s^{-1}, corresponding to the column efficiency of 2224 plates/m. The polarity of stationary phase is an important index to judge the selectivity and separation performance of column. It can be measured by using the McReynolds constants of five probe compounds, including benzene (X'), 1-butanol (Y'), 2-pentanone (Z'), 1-nitropropane (U') and pyridine (S') at 120 °C. The McReynolds constants of C4A-PEG-2PTSC, HP-35 and PEG-20M columns were listed in Table 1. As shown, the average value of C4A-PEG-2PTSC column was 383, exhibiting moderate polarity.[31-34]

Separation performance and retention behaviors

The Grob mixture including 12 analytes is a diagnostic mixture used to evaluate the overall separation performance of
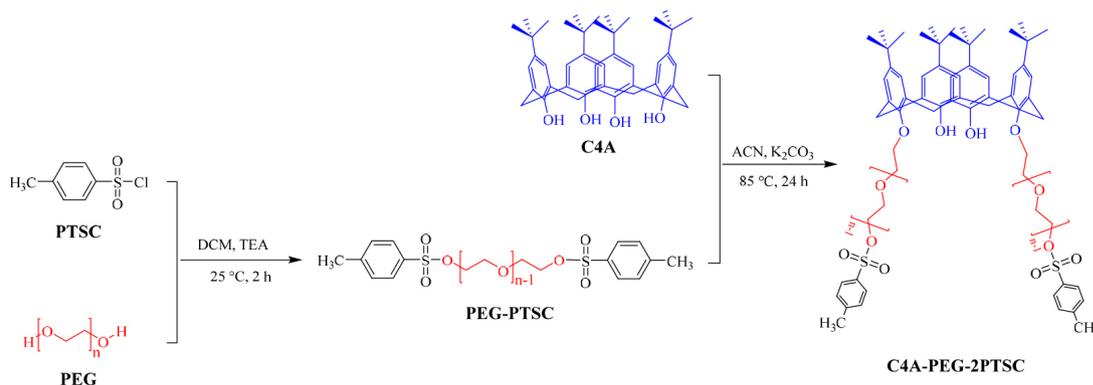
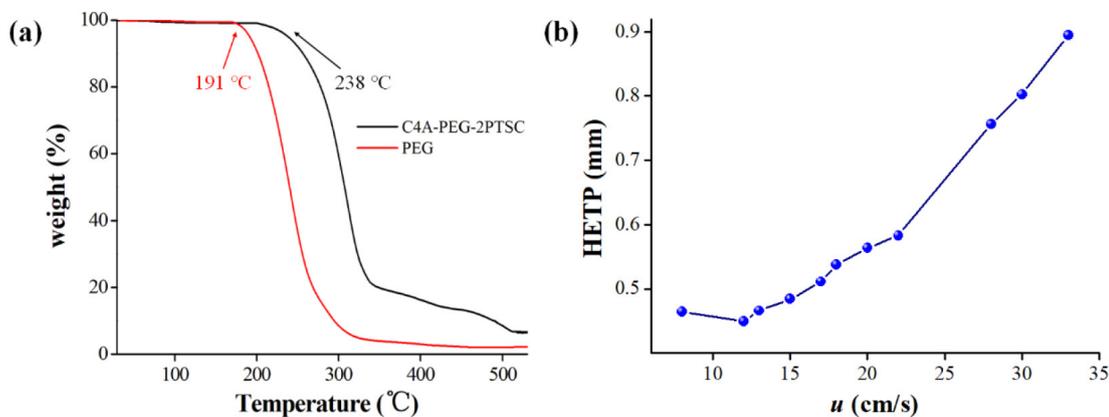*Figure 1. Synthesis of the C4A-PEG-2PTSC stationary phase*

Figure 2. *(a) TGA for C4A-PEG-2PTSC and PEG stationary phases; (b) Golay curve of the C4A-PEG-2PTSC column was determined by 1-octanol*

Table 1. McReynolds constants of the C4A-PEG-2PTSC, HP-35 and PEG-20M columns

Stationary phases	X'	Y'	Z'	U'	S'	General polarity	Average
C4A-PEG-2PTSC	242	472	292	490	417	1913	383
HP-35	105	174	149	232	182	842	168
PEG-20M	428	520	352	909	485	2694	539

X': benzene; Y': 1-butanol; Z': 2-pentanone; U': 1-nitropropane; S': pyridine. Temperature: 120 °C.

chromatographic column. Figure 3 presented the separation of Grob mixture on the C4A-PEG-2PTSC column in comparison to that on the C4A-C10,[35] HP-35 and PEG-20M columns. Obviously, most components were well resolved and achieved good peak shapes except dicyclohexylamine (peak 10) on the C4A-PEG-2PTSC column, which probably due to its irreversible adsorption with the active site on the column. The C4A-PEG-2PTSC column had higher resolution for the pair of *n*-undecane/*n*-nonanal/1-octanol (peak 2/3/4) with close boiling points (b.p. 190-196 °C) than the C4A-C10 column, and the component 2,3-butanediol (peak 5) had a prolonger retention trend and obtained a sharp peak on the C4A-PEG-2PTSC column which suggested the H-bonding and dipole-dipole interactions between stationary phase and analytes. Furthermore, the C4A-PEG-2PTSC column presented outstanding separation ability for 2,6-dimethylaniline/2,6-dimethylphenol/2-ethylhexanoic acid (peaks 9/11/12) that some of these components were tailed on other columns. Significantly, the C4A-PEG-2PTSC column presented sharp and symmetrical peak shape for 2-ethylhexanoic acid (peak 12), indicating its good column inertness.[36-39] The results suggested the modified C4A-PEG-2PTSC stationary phase had better film-forming ability and resolving capability than C4A-C10 stationary phase.

To more comprehensively examine the separation performance and retention behavior of C4A-PEG-2PTSC column, the complex mixture of 23 analytes with diverse types was used including *n*-alkanes, bromoalkanes, esters, ketones, alcohols, alkylbenzenes, halogenated benzenes and anilines, and compared with the results on the HP-35 and PEG-20M columns. As shown in Figure 4, the C4A-PEG-2PTSC column exhibited high resolution ($R >$ 1.5) of all the analytes ranging from non-polar to polar nature over the other commercial columns. Among them, some pairs of components coeluted or partially overlapped on the other columns, including 1,3,5-trimethylbenzene/1-heptanol (peaks 6/13), 1-bromoheptane/1,2,3-trimethylbenzene (peaks 7/9), *n*-tridecane/methyl nonanoate (peaks 11/14) and 2,6-dimethylaniline/2,5-dimethylaniline (peaks 20/21) on the HP-35 column, 1,2,3-trimethylbenzene/1-hexanol (peaks 9/10) and 1,4-dichlorobenzene/1-heptanol (peaks 12/13) on the PEG-20M column.

In addition, the elution order of some analytes did not follow their boiling point order on the C4A-PEG-2PTSC column, such as the

pairs of *n*-decane/ethylbenzene (peaks 1/2; b.p., 175 °C/136 °C) and *n*-tridecane/1,4-dichlorobenzene (peaks 11/12; b.p., 234 °C/174 °C), which can be attributed to the aromatic ring of C4A-PEG-2PTSC offered the π-π stacking interactions, and the stronger retention for 1-nonanol than for the *n*-pentadecane (peaks 16/17; b.p., 268 °C/215 °C) can be attributed to the H-bonding and dipole-dipole interactions between them. Interestingly, the C4A-PEG-2PTSC column presented different selectivity and retention behaviors for the mixture in comparison to the HP-35 column, such as the 2-heptanone and 2-octanone in the pairs of *n*-decane/2-heptanone (peaks 1/4; b.p., 174 °C/149 °C) and 1-bromoheptane/2-octanone (peaks 7/8; b.p., 178 °C/173 °C) had longer retention time on the C4A-PEG-2PTSC column than on the HP-35 column, suggesting the separation is mainly due to the dipole-dipole interaction, and the prolonged retention of *o*-toluidine in the pair of 1-nonanol/*o*-toluidine (peaks 17/19; b.p., 213 °C/200 °C) may derive from π-π interaction. In brief, the C4A-PEG-2PTSC column presented good separation ability and different retention interactions for the analytes of diverse polarities.

The high resolution and selectivity of stationary phase is significant for isomer mixtures in the petrochemical industry and environmental analysis. Thus, some aliphatic and aromatic isomers were performed on the C4A-PEG-2PTSC column. Figure 5(a)-5(h) exhibited the separations of analytes with different polarity, including alkylated benzenes, naphthalenes, halogenated benzenes, benzaldehydes, phenols and alcohols. Clearly, the C4A-PEG-2PTSC stationary phase provided efficient separations for the non-polar aromatic isomers, containing trimethylbenzene (Figure 5a), methylnaphthalene (Figure 5b) and dimethylnaphthalene (Figure 5c). Meanwhile, it achieved baseline separation for halogenated benzenes ($R > 1.5$) with the symmetrical peak shape, covering dichlorobenzene (Figure 5d), dibromobenzene (Figure 5e), trichlorobenzene (Figure 5f), nitrochlorobenzene (Figure 5g) and nitrobromobenzene (Figure 5h). Notably, the baseline separation ($R > 1.5$) was obtained for *m*-/*p*-dichlorobenzene and *m*-/*p*-dibromobenzene even though their boiling points differed by less than 1°C.

This distinguishing ability was mainly due to the slightly different π-π interactions between them. Figure 6 presented the separations for the challenging isomers of nitrobenzaldehyde (Figure 6a), cyanobenzaldehyde (Figure 6b), dichlorobenzaldehyde
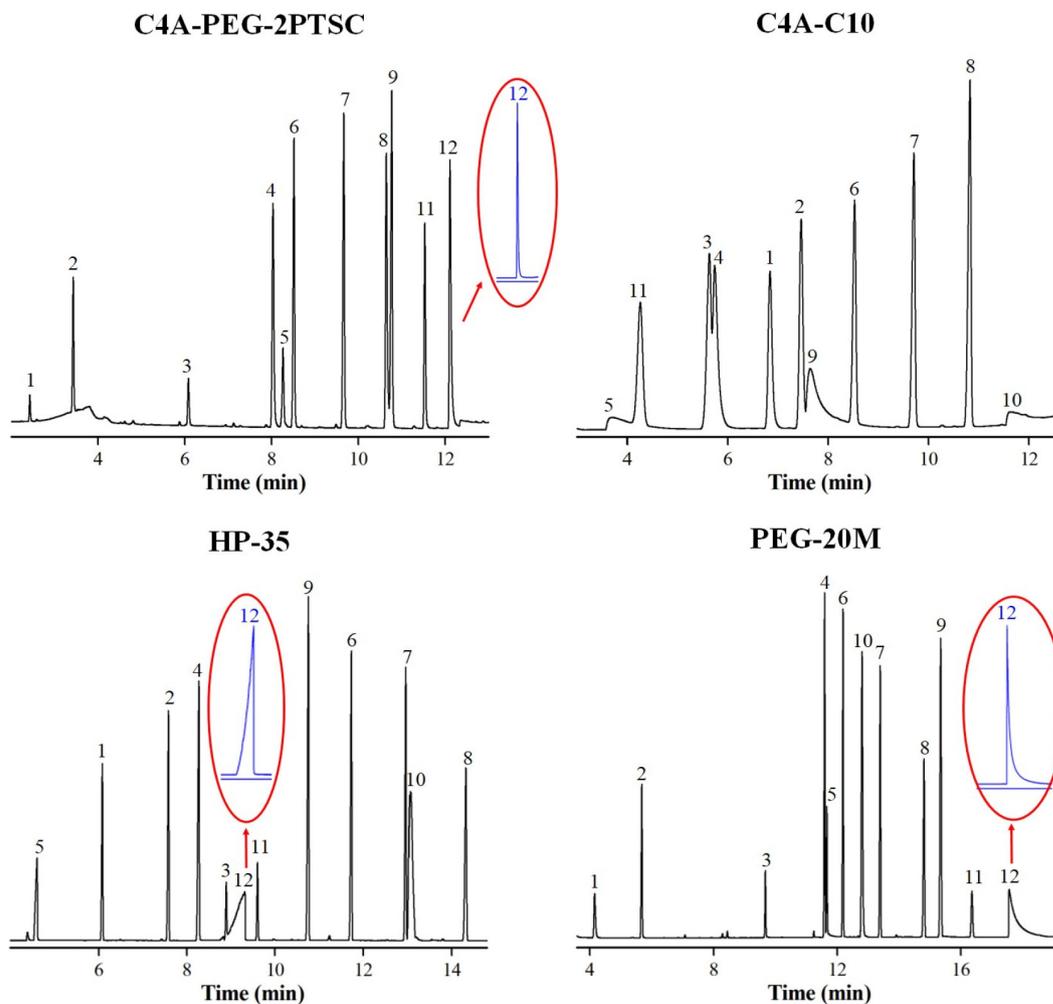
C4A-PEG-2PTSC

C4A-C10

HP-35

PEG-20M

Figure 3. Separations of Grob mixture on the C4A-PEG-2PTSC, C4A-C10, HP-35 and PEG-20M columns. Peaks: (1) n-decane, (2) n-undecane, (3) nonanal, (4) 1-octanol, (5) 2,3-butanediol, (6) methyl decanoate, (7) methyl undecanoate, (8) methyl dodecanoate, (9) 2,6-dimethylaniline, (10) dicyclohexylamine, (11) 2,6-dimethylphenol, (12) 2-ethylhexanoic acid. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹
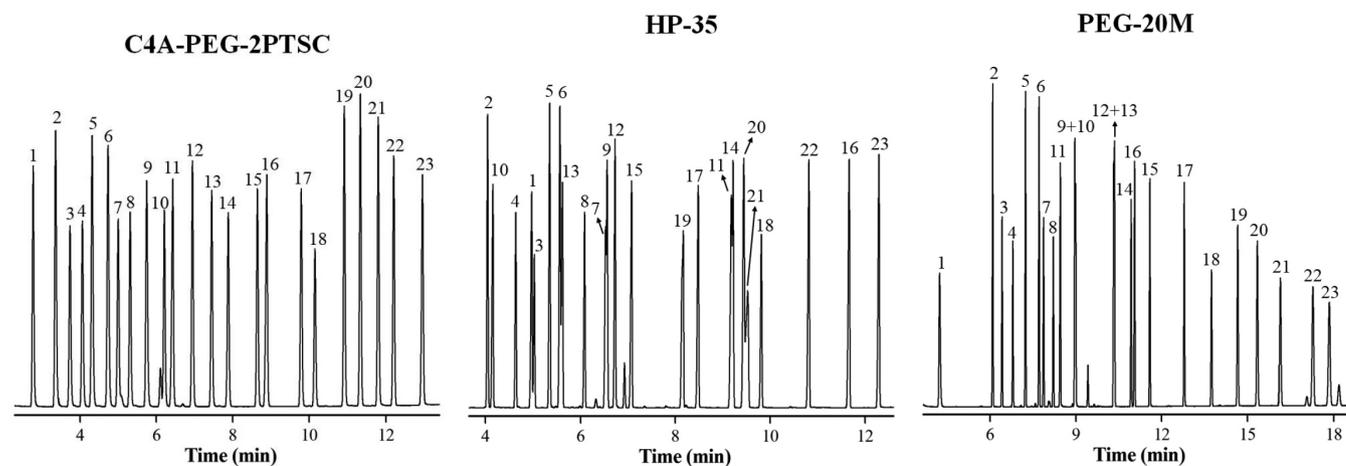
C4A-PEG-2PTSC

HP-35

PEG-20M

Figure 4. Separations of the mixture of 23 analytes of diverse types on the C4A-PEG-2PTSC, HP-35 and PEG-20M columns. Peaks: (1) n-decane, (2) ethylbenzene, (3) 1-bromohexane, (4) 2-heptanone, (5) n-propylbenzene, (6) 1,3,5-trimethylbenzene, (7) 1-bromoheptane, (8) 2-octanone, (9) 1,2,3-trimethylbenzene, (10) 1-hexanol, (11) n-tridecane, (12) 1,4-dichlorobenzene, (13) 1-heptanol, (14) methyl nonanoate, (15) 1-octanol, (16) n-pentadecane, (17) 1-nonanol, (18) 1,2,3-trichlorobenzene, (19) o-toluidine, (20) 2,6-dimethylaniline, (21) 2,5-dimethylaniline, (22) 4-chloronitrobenzene, (23) 1-dodecanol. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹

(Figure 6c), dimethylphenol (Figure 6d) and butanol (Figure 6e). These analytes are difficult to separate well and prone to be seriously peak tailed in GC analyses. As shown, all the analytes

obtained sharp and symmetrical peak shapes, especially the peaks of dimethylphenols and butanol. Thus, the outstanding separation performance of the C4A-PEG-2PTSC column for the critical isomers
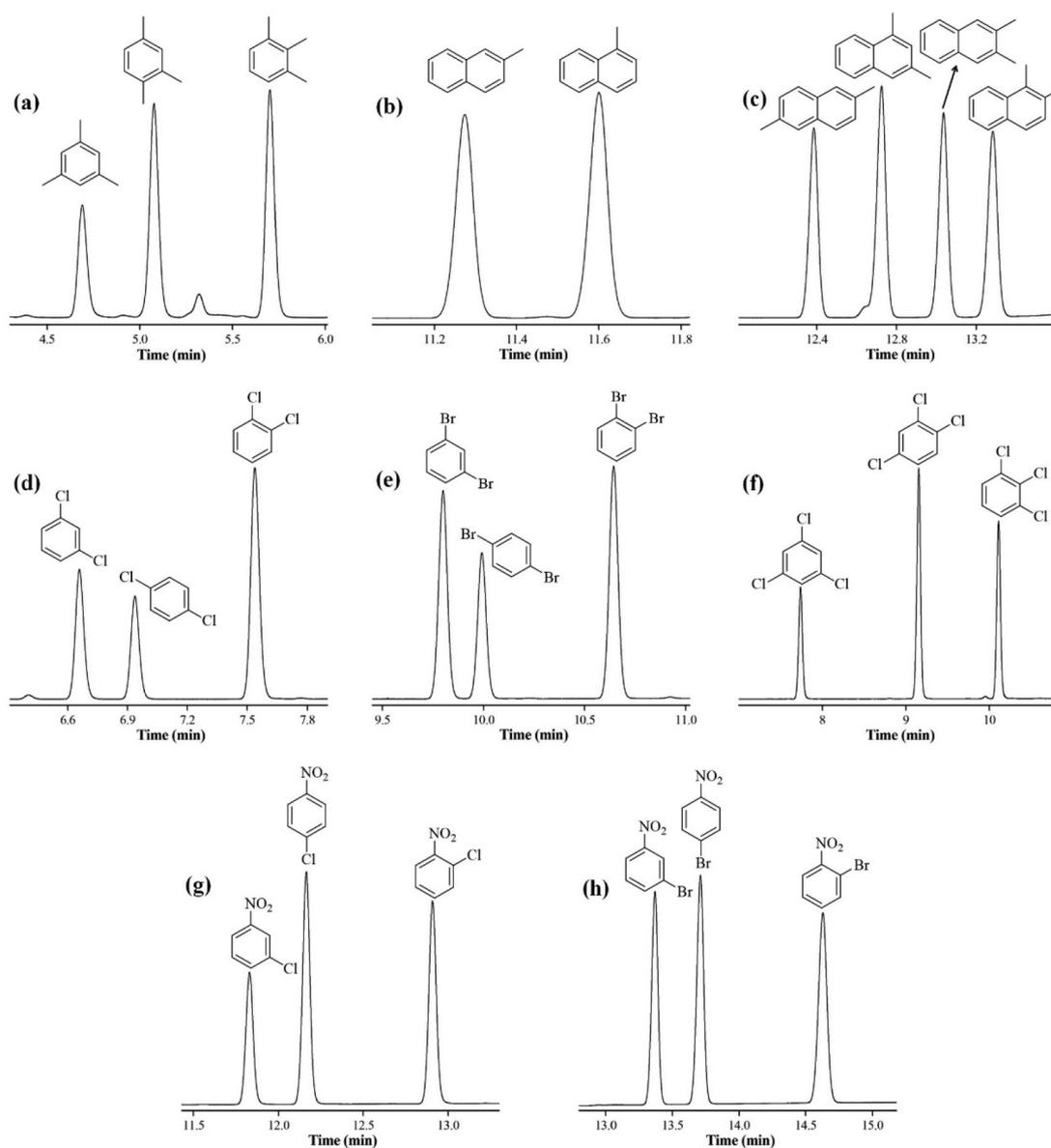
Figure 5. *Separations of isomer mixtures of (a) trimethylbenzene, (b) methylnaphthalene, (c) dimethylnaphthalene, (d) dichlorobenzene, (e) dibromobenzene, (f) trichlorobenzene, (g) nitrochlorobenzene and (h) nitrobromobenzene on the C4A-PEG-2PTSC column. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹*

may be attributed to its unique structure and multiple interactions, such as van der Waals force, dipole-dipole, H-bonding and π-π interactions. The above results showed that the C4A-PEG-2PTSC column has good chromatographic selectivity for both nonpolar and polar analytes.

Aromatic amines are acknowledged as the poisonous compounds and will pose a threat to human health and environment. These compounds are commonly found in chemicals, pharmaceuticals and textile dyes. Figure 7 showed the separations of toluidine and xylidine isomers on the C4A-PEG-2PTSC column in comparison to that on the HP-35 column. Significantly, the isomers of toluidine and xylidine obtained baseline separation (R > 1.5) on the C4A-PEG-2PTSC column, and the resolution of aniline analytes on HP-35 column were significantly lower than that on C4A-PEG-2PTSC column. The separation ability of the C4A-PEG-2PTSC column may be owing to the aromatic skeleton, PEG chains and PTSC terminated groups made the contribution in the GC separations. In addition, we investigated the separation performance of C4A-PEG-2PTSC stationary phase for

cis-/trans- isomers, involving alkenes, furans, naphthalenes, heterocycles and alcohols. As shown in Figure 8, the C4A-PEG-2PTSC column presented a good performance for all the isomers with little discrepancy in natures and structures.

In order to further verify the separation ability of the C4A-PEG-2PTSC column in the practical analysis, this work applied it for the detection of tracing isomer impurities in the commercial reagent samples, and the HP-35 column were used as the reference. Figure 9 exhibited the results for the determination of the reagent samples including 1,2,4-trichlorobenzene, 2,4-dimethylaniline, *m*-xylene and *o*-xylene.

Table 2 listed the content of isomer impurities by peak area normalization method. Compared with commercial HP-35 column, the C4A-PEG-2PTSC column also had excellent ability for detection of isomer impurities. In the Table 2, the measured purity of practical samples was in agreement with their label purity for the above analytes, proving the potential application of the C4A-PEG-2PTSC column for practical sample analysis in GC separations.
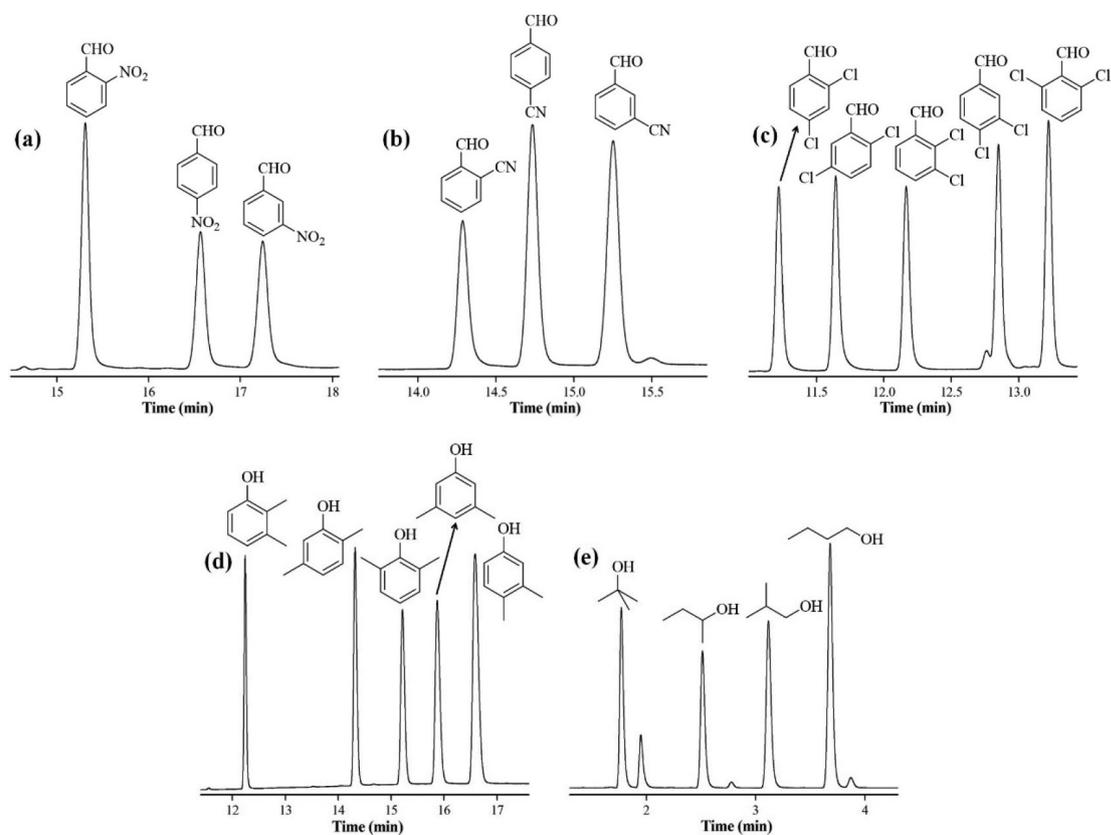
Figure 6. *Separations of isomer mixtures of (a) nitrobenzaldehyde, (b) cyanobenzaldehyde, (c) dichlorobenzaldehyde, (d) dimethylphenol and (e) butanol on the C4A-PEG-2PTSC column. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹*
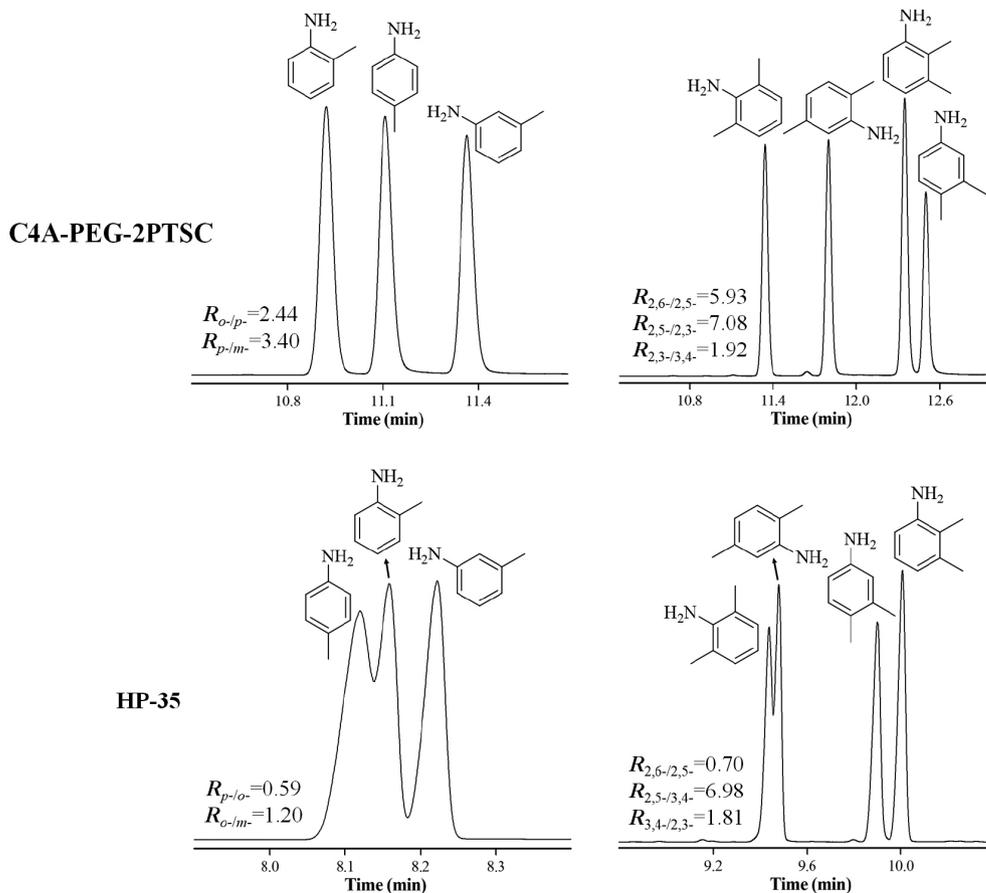

Figure 7. *Separations of toluidine and xylidine isomers on the C4A-PEG-2PTSC, and HP-35 columns. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹*
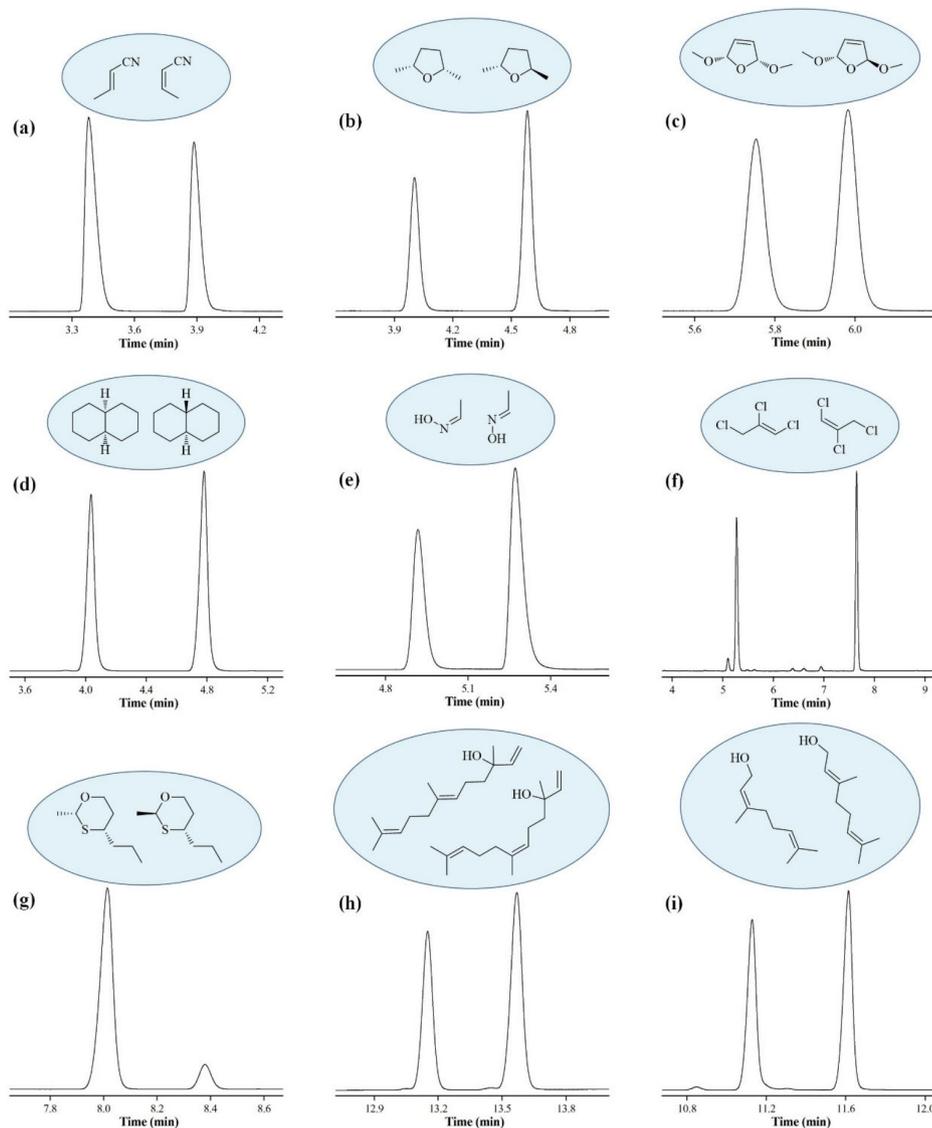
Figure 8. *Separations of cis-/trans- isomers of (a) 2-butenenitrile, (b) 2,5-dimethyltetrahydrofuran, (c) 2,5-dihydro-2,5-dimethoxyfuran, (d) decahydronaphthalene, (e) acetaldoxime, (f) 1,2,3-trichloropropene, (g) 2-methyl-4-propyl-1,3-oxathiane, (h) nerolidol and (i) nerol/geraniol on the C4A-PEG-2PTSC column. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹*
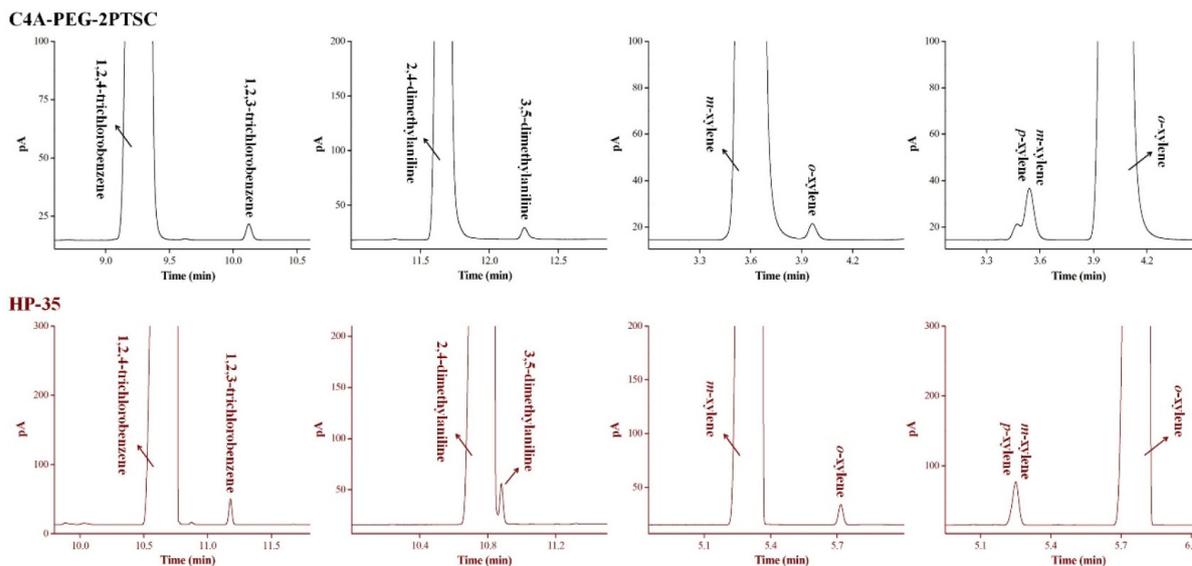

Figure 9. *Applications of the C4A-PEG-2PTSC and HP-35 columns for the determination of minor isomer impurities in the real samples of 1,2,4-trichlorobenzene, 2,4-dimethylaniline, m-xylene and o-xylene. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹*

Table 2. Results for the detection of isomer impurities in the commercial reagent samples on the C4A-PEG-2PTSC and HP-35 columns

Column	Samples	Labeled Purity	Measured Purity	Isomer Impurity	Content
C4A-PEG-2PTSC	1,2,4-trichlorobenzene	99%	99.62%	1,2,3-trichlorobenzene	0.23%
	2,4-dimethylaniline	99%	99.06%	3,5-dimethylaniline	0.35%
	m-xylene	99%	99.74%	*o*-xylene	0.16%
	o-xylene	99%	99.09%	*m*-xylene, *p*-xylene	0.73%
HP-35	1,2,4-trichlorobenzene	99%	99.41%	1,2,3-trichlorobenzene	0.28%
	2,4-dimethylaniline	99%	99.53%	3,5-dimethylaniline	0.46%
	m-xylene	99%	99.73%	*o*-xylene	0.17%
	o-xylene	99%	98.78%	*m*-xylene, *p*-xylene	0.73%
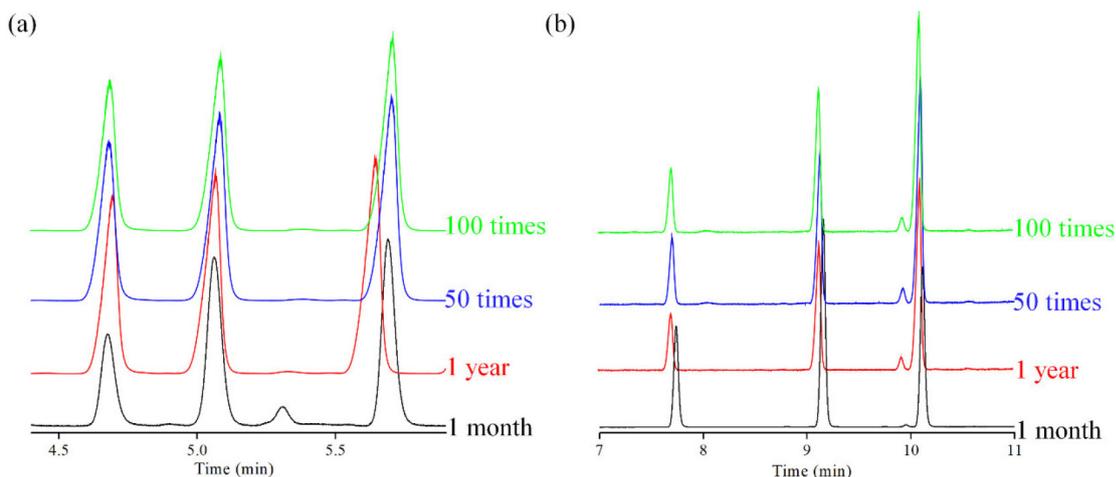
Figure 10. The reproducibility and stability of the C4A-PEG-2PTSC column for the separation of (a) trimethylbenzene and (b) trichlorobenzene isomers. Temperature program: 40 °C (keep 1 min) up to 160 °C (keep 5 min) at 10 °C min⁻¹ and flow rate: 0.6 mL min⁻¹

Table 3. Results for the detection of isomer impurities in the commercial reagent samples on the C4A-PEG-2PTSC column

Analytes	RSD	
	50 times	100 times
1,3,5-trimethylbenzene	0.065%	0.057%
1,2,4-trimethylbenzene	0.064%	0.055%
1,2,3-trimethylbenzene	0.056%	0.049%
1,3,5-trichlorobenzene	0.014%	0.022%
1,2,4-trichlorobenzene	0.008%	0.013%
1,2,3-trichlorobenzene	0.007%	0.009%

Reproducibility and stability of the C4A-PEG-2PTSC column

The reproducibility and stability of the C4A-PEG-2PTSC column was investigated. Figure 10 showed the chromatograms of trimethylbenzene and trichlorobenzene obtained when the C4A-PEG-2PTSC column was used for 1 month and 1 year, and after the column was subjected to 50 and 100 injections. There was no obvious change in the retention time of trimethylbenzene and trichlorobenzene, and the RSD of the retention time after the column was subjected to 50 and 100 injections was less than 0.07% (Table 3), indicating the good reproducibility and stability of the C4A-PEG-2PTSC column.

CONCLUSION

This work presents the investigation of the C4A-PEG-2PTSC as stationary phase in GC analyses. The C4A-PEG-2PTSC column

had good separation ability and column inertness for various types of analytes and isomers, including Grob mixture, the mixture of 23 analytes, aliphatic and aromatic analytes. The high selectivity of C4A-PEG-2PTSC stationary phase may drive from its distinctive molecular structure and rich interactions involving Van der Waals forces, dipole-dipole, H-bonding and π-π interactions. This work demonstrated its good application potential in GC separations.

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