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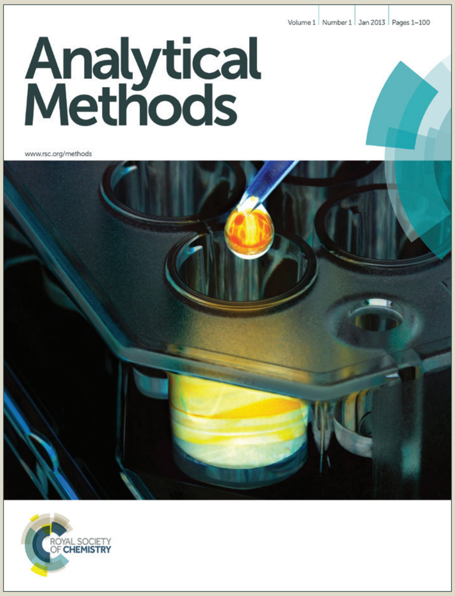

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Synthesis and Characterization of Diphenyl–Phenyl Polysiloxane as High-temperature Gas Chromatography Stationary Phase

Pengchao Zhao, Shuang Teng, Miao Yu, Na Niu, Xinxin He, Bo Wu*
School of Chemistry and Chemical Engineering, Shandong University, 27 Shanda South Road, 250100, China
* To whom the correspondence should be addressed:
Bo Wu
Tel: + 86-531-88364464
Fax: + 86-531-88364464
E-mail: wubo@sdu.edu.cn

Abstract

A new type of copolymer diphenyl–phenyl polysiloxane (DPPP) was synthesized and coated on the inside of fused-silica capillary columns for use as a novel stationary phase in gas chromatography (GC). The thermal stability, selectivity, polarity, column efficiency, and maximum allowable temperature for these capillary columns were characterized. The obtained results indicated that the prepared columns exhibited higher column efficiency (3560 plates/m to 3630 plates/m). The excellent film-forming capability in the inner surface of fused-silica capillary columns was proven by the analysis of Grob test compounds. The maximum allowable temperature was determined to be 360 °C, which indicated that the copolymer was highly suitable for high-temperature separation. In addition, superior peak shapes were observed when the DPPP column was used to separate substituted benzene mixtures and polycyclic aromatic hydrocarbons, which suggests a great potential for application in GC analyses.

1. Introduction

High-temperature gas chromatography (HTGC) is known to be suitable for analyzing high-molecular-weight and thermostable organic compounds for its thermal stability and high efficiency [1]. The most important component of gas chromatography (GC) analyses is the chromatographic column, the core of which is a stationary phase that determines the thermal stability of a GC capillary column. A stationary phase with high thermal stability is required to accomplish high-temperature separation. While some new stationary phases have been widely concerned in recent years, such as Metal-Organic Framework MIL-101 used for separation of xylene isomers [2] and Zeolitic Imidazolate Framework-8 used for molecular sieving of branched alkanes from linear alkanes with large diversity in structures and pore sizes, and selective penetrations [3], over the past decades, modified polysiloxanes have been extensively used as stationary phases because of their film-forming capability, wide operational temperature, and high thermal stability in GC [4, 5]. A new type of non-extractable methylphenylpolysiloxane with 4% vinyl was synthesized by Peaden et al. in 1982. This material then became a widely used GC stationary phase. Cross-linking of the vinyl group enables the stationary phase to be utilized at temperatures of up to 400 °C [6]. Modified polysiloxanes with biphenyl [7], dicyanobiphenyl [8], methoxylphenyl [9], and naphthyl [10] groups were subsequently developed by Lee et al. These cross-linked stationary phases possessed improved polarity and unique selectivity for environmental pollutants, such as polycyclic aromatic hydrocarbons (PAHs). However, these modified stationary phases synthesized by Lee et al. could only be used at temperatures below 280 °C. Remarkable improvement was recently achieved by Mayer et al., who have synthesized polysiloxane consisting of 75% diphenyl and 25% dimethyl (SOP-75); they used the polysiloxane to coat fused-silica capillary columns for use in high-temperature GC analyses [11]. This stationary phase offered specific selectivity and thermal stability at temperatures of up to 400 °C [11]. Similarly, more recently modified polysiloxanes containing 50% n-octylmethyl-50% diphenyl (SOP-50-Octy) [12] and trifluoropropyl [13] have been utilized as GC stationary phases. These two types of stationary phases exhibited unique selectivity and could be used at high operating temperature ranges.

In previous studies, introducing a phenyl group to polysiloxane can improve polarity and resistance to oxidation. Given that phenyl groups are easily polarized, dipole–dipole and dispersion forces can be formed between stationary phases and solutes [7]. Multiphenyl polysiloxane with bulky mobile π-bonding electrons thus exhibit an evident advantage over previous phases. Such advantages are important for separation. Moreover, with the cross-linkable vinyl group, the obtained columns can achieve a higher operating temperature [14]. Therefore, combining the merits of thermal stable polysiloxane with the polarizable multiphenyl–phenyl groups endows this type of stationary phase with outstanding heat resistance and unique selectivity.

In this study, the polarizable compound DPPP, which contains a diphenyl–phenyl functional group, was synthesized and used as the high-temperature stationary phase. ^{1}H nuclear magnetic resonance spectroscopy (^{1}HNMR), infrared (IR) spectroscopy, and thermogravimetric analysis (TGA) were used to characterize the polymer composition and structure. The fused-silica capillary columns coated with this newly synthesized polymer were evaluated in terms of column efficiency, polarity, working temperature range, and separation efficiency. Moreover, the applications of such columns in the analysis of substituted benzenes and high-boiling-point compounds, such as PAHs, were described. The obtained results indicate a great potential of DPPP in practical application as stationary phases for HTGC.

2. Experimental

2.1 Chemicals

All reagents were of analytical grade. The IR spectra of the compound were recorded as thin films for liquid compounds on a Nicolet spectrometer (Magna550). ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a DPX 400 spectrometer (Bruker Analytische Messtechbik, Germany). All NMR spectra were determined in $CDCl_3$ at ambient temperature. To evaluate the thermal stability of DPPP, the TGA of DPPP was performed on an LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China). Molecular weight and its distribution were determined by gel permeation chromatography (Waters 515 HPLC) at room temperature.

2.2 Synthesis of 3, 4-diphenylcyclopentadienone

A mixture of benzil (7.0 g, 0.033 mol) and acetone (1.9 g, 0.033 mol) was dissolved in stirred ethanol (50.0 mL) under nitrogen protection. A small amount of KOH in ethanol (1.0 g of potassium hydroxide dissolved in 5.0 mL ethanol) was added dropwise into the solution over a period of 1 h with stirring at 80 °C. The reaction proceeded for 15 min, and then the mixture was filtered after cooling. The crude product was re-crystallized from the solvent mixture of ethanol/toluene (V/V=1:1) to obtain 6.5 g of bright black crystals at a yield of approximately 85.1%.

2.3 Procedure for the preparation of DPPP

Methyl vinyl polysiloxanes with different vinyl contents of 10%, 20%, and 25% were obtained according to Reference [15]. DPPP was prepared according to the procedure described in Fig. 1. Appropriate amounts of methyl vinyl polysiloxane and 3, 4-diphenylcyclopentadienone (in particular, a small percentage of the vinyl group was retained in each polymer mixture to facilitate cross-linking, as described in the Reference [16]) were dissolved in diphenyl ether (50.0 mL) and heated at 259 °C for 28 h under nitrogen. The polymerization reaction was terminated when bubbles stopped evolving. The solution was poured into a separatory funnel, and the diphenyl ether layer was removed at 110 °C. Finally, a highly viscous polymer was obtained. For purification, the polymer was dissolved in toluene, precipitated with methanol five times, and dried in vacuum at 50 °C to obtain a clear, pale yellowish gum at a yield of approximately 78.2%. The products were labeled DPPP-10, DPPP-20, and DPPP-25 according to vinyl group content.

The structures of the products were analyzed by means of IR and NMR. The IR data of DPPP-25 (cm^{-1}, KBr) are as follows: Si-Me$_2$, 1264.8 (Si-Me), 1094.0, 803.8 (Si-O-Si), 853.4, and 739.8 (Si-Me$_2$); 3054.4, 1599.5, and 1018.5 (Vinyl); 1421.8 (Si-Ph); and 896.0 (biphenyl–phenyl). The chemical compositions of 7.84%, 15.54%, and 21.92% diphenyl–phenyl group in DPPP were roughly calculated from the integration of the ^{1}H NMR spectra. The contents of the remaining vinyl groups were determined to be 1.73%, 2.66%, and 2.53%, which are in a good agreement with the theoretical calculation. The results of gel permeation chromatography showed the number average molecular weight (M_n) of 1.21×10^5 to 1.41×10^5 with the average molecular weight (M_w/M_n) ratio of 1.42 to 1.73.

2.4 Preparation of chromatographic column

The fused-silica capillary column produced in our laboratory was treated according to previously described methods [17, 18]. The fused-silica capillary tube with an inner diameter of 0.25 mm was filled with 10% (w/v) sodium hydroxide in ethanol and then etched for 24 h. The etched column was consecutively rinsed with water, diluted with hydrochloric acid (1/3, V/V), water, and methanol (15 mL each), and finally dried under nitrogen at 250 °C for 2 h. After washing with 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane in dichloromethane (10%, w/v), the treated tubes were dried under nitrogen at room temperature for 2 h to remove the residual solvent from the column. Then, both ends of the capillary column were sealed and deactivated at 420 °C for 2 h. The ends were then rinsed with 5 mL of dichloromethane and dried under nitrogen at 250 °C for 2 h. The columns were statically coated with a solution of 0.5% (w/v) of DPPP in dichloromethane with a film thickness of 0.25 μm. Three columns were prepared and labeled as DPPP-10, DPPP-20, and DPPP-25. After the coating procedure, the capillary columns were conditioned at 50 °C for 0.5 h under a nitrogen flow. The temperature was then raised to 360 °C at a rate of 2 °C/min and then maintained at 360 °C for 12 h.

2.5 Evaluation of chromatographic column

All analyses were conducted on a GC-2014C (Shimadzu), equipped with a flame-ionization detector. High-purity nitrogen was used as carrier gas at a linear velocity of 13.5 cm/s (except for the separation of Grob test mixtures, which is 10 cm/s). Column efficiency was evaluated by measuring the number of plates per meter for naphthalene at 120 °C. The polarity of the stationary phase was characterized by McReynolds constants. The injection split ratio was 30 to 1. Unless otherwise specified, both injector and detector temperatures were set to 350 °C.

3. Results and Discussion

3.1 Column efficiency

Column efficiencies were evaluated by measuring the number of plates per meter for naphthalene at 120 °C. The chromatographic properties of the newly prepared columns are summarized in Table 1. We found the column efficiencies of the DPPP-10, DPPP-20, and DPPP-25 columns to be about 3500 plates/m to 3800 plates/m. Data indicate that the DPPP-10, DPPP-20, and DPPP-25 columns possessed high efficiency. The coating efficiency of the new stationary phases exceeded 85%, which implies good film-forming capability. The retention factor of DPPP-25 was the highest and was superior to those of the others. The column efficiency of DPPP-20 was similar to that of DPPP-25. Nevertheless, we found that when the diphenyl–phenyl group content reached up to 30% in the polymer, a solid, instead of a gum product, was obtained at room temperature. The prepared solid polymer was similar to tetraphenyl polymer in that was unsuitable for low-temperature chromatographic separation [7]. These results were consistent with those previously reported by Lee et al [10]. However, the low diphenyl–phenyl contents could not improve selectivity. Therefore, we selected the DPPP-25 stationary phase for further studies.

3.2 Polarity

To investigate the polarity of the new stationary phases, the Rohrschneider–McReynolds constants were quantitatively measured. Each probe molecule interacted with the stationary phase in a specific manner, which included the following: X′- dispersive interactions; Y′- proton donor and acceptor capabilities plus dipolar interactions; Z′- dipolar interactions plus weak proton acceptor, but without proton donor capabilities; U′- dipolar interactions; and S′- strong proton acceptor capabilities [19]. Table 2 lists the Rohrschneider–McReynolds constants on the three new stationary phases and OV-17 (50% phenyl–50% methyl polysiloxane) at 120 °C. The elution sequence of the McReynolds probes was Y′→X′→Z′→U′→S′. Table 2 shows that the polarity of the DPPP-25 column was higher than those of the DPPP-10 and DPPP-20 columns but similar to that of the OV-17 column. The results indicate that the polarities of the DPPP columns were dominated by the diphenyl–phenyl group. On the basis of the Z′ value, which is related to the polarizability and partial dipolar characteristic of the stationary phases [20], we find that the polarizability of the DPPP-25 column was similar to that of OV-17 and higher than those of others. Higher McReynolds constants for proton donor (Y′, butanol) and proton acceptor (S′, pyridine) suggest that the DPPP-25 stationary phase could achieve strong retention of polar compounds.

3.3 Selectivity

Grob test mixtures were used to evaluate the overall characteristics of the newly prepared capillary columns. The chromatograms of the Grob test mixtures are illustrated in Fig. 2. As shown in Fig. 2, the Grob test mixtures were well separated, and symmetrical peaks were obtained. These findings indicate that the new DPPP-25 stationary phase can deactivate the inner surface of the column and has good film-forming capability. These findings are consistent with the gummy properties of the new DPPP-25 stationary phase, which can afford high column efficiency [21]. The elution order of Grob test mixtures on the DPPP-25 stationary phase was similar to that on the SOP-75 column [22]. Notably, 2,6-dimethyl aniline was eluted after 2,6-dimethylphenol, which implies that the new stationary phase retained alkaline analytes more strongly than acidic ones. Additionally, the tailor factor of 1-octanol (4) on the DPPP-25 column was close to 1.12, which indicates good deactivation of surface silanol groups on the fused-silica capillary in the DPPP-25 column.

3.4 Maximum allowable temperature

To evaluate the maximum allowable temperature of the DPPP-25 column, TGA and column bleeding test were performed. A 10 mg sample was heated from 25 °C to 700 °C at a rate of 10 °C/min under helium. The TGA curve of DPPP-25 is shown in Fig. 3. DPPP-25 began to decompose slightly at 380 °C and then dramatically decomposed between 400 °C and 550 °C. Column bleeding was measured by programming the DPPP-25 column from 250 °C to 400 °C at a heating rate of 4 °C/min. The results reveal that the DPPP-25 column began to bleed at 360 °C and that the baseline drift was 4×10^{-15} A. We can therefore conclude that DPPP-25 can endure high temperatures of up to 360 °C, which is consistent with the TGA results. The DPPP-25 column exhibited higher thermostability than commercial stationary phase cross-linked methylphenylsilicone with thermal stability of up to 320 °C [16].

3.5 Application

The gas chromatographic separation of substituted benzene mixtures on the DPPP-25 column is illustrated in Figure 4. The chromatographic relative retention value of all three DPPP columns for the separation of the substituted benzene mixtures are shown in Table 3. As shown in Fig. 4, the substituted benzene mixtures were well separated, and sharp symmetrical peaks were observed. All di-substituted and tri-substituted benzene isomers were baseline separated, indicating that the π-π interaction between the solutes and the stationary phase served an important function in the separation mechanism. The substantially improved selectivity and separation power of the new stationary phase may be related to the increased polarizability of the diphenyl–phenyl functional group with strong electron-donating capability. Therefore, the DPPP-25 column can potential be used as a GC stationary phase for the analysis of complex samples.

The superior separation capability of the DPPP-25 stationary phase with a unique molecule structure was exemplified in the analysis of high-boiling-point organic compounds, such as PAHs. A representative chromatogram of PAHs separated on the DPPP-25 column is shown in Fig. 5. These compounds were eluted in the order of their increasing dispersion force, which was in agreement with dicyanobiphenyl polysiloxane [8]. This result may be attributed to the participation of the diphenyl–phenyl group, which contains conjugated π-bonds. Given that most of these PAHs are major environmental pollutants, the DPPP-25 column can be widely used for environmental monitoring.

4. Conclusions

This work described a synthetic method for producing methyl DPPP and the use of this material as a novel GC stationary phase. Polysiloxane with polarizable diphenyl functional group, when used as a stationary phase for GC, exhibited superior film-forming capability and higher column efficiency. Moreover, the sum of Rohrschneider–McReynolds constants indicated that the diphenyl–phenyl group significantly influenced the polarity of the DPPP stationary phases. In addition, the results of Grob testing indicated that greater π-π interaction between the solutes and the stationary phase occurred in the DPPP-25 column. Furthermore, the superior selectivity of the DPPP-25 column can be used to separate analytes, including substituted benzenes, aromatic isomers, and PAHs, within a wide range of polarity. This extensive applicability suggests that the DPPP-25 stationary phase has considerable potential in HTGC separation.

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Table 1. The chromatographic properties of diphenyl-phenyl polysiloxane columns at 120 ºC.

Column numbers	Stationary phases	Dimensions length L (m) × i.d. (mm)	Column efficiency (plates/m)	Retention factor (k)	Coating efficiency (%)
1	DPPP-10	20 × 0.25	3562	4.10	85.5
2	DPPP-20	20 × 0.25	3788	3.47	86.9
3	DPPP-25	20 × 0.25	3762	4.46	85.9

Table 2. The McReynolds constants of diphenyl-phenyl polysiloxane stationary phases at 120 ºC

Stationary phases	Benzene (X′)	Butanol (Y′)	2-Pentanone (Z′)	Nitropropane (U′)	Pyridine (S′)	Sum
DPPP-10	97	159	126	132	93	607
DPPP-20	113	160	166	154	131	724
DPPP-25	122	168	157	190	195	832
OV-17 (ref. 17)	119	158	162	243	174	856

Table 3. Retention factors (*k*) and relative retention values (*α*) of disubstituted benzene isomers on the three columns.

Sample	Stationary phase	Peak order	Temperature (ºC)	Retention factor (*k*)			Relative retention (*α*)	
				k_1	k_2	k_3	$\alpha_{2/1}$	$\alpha_{3/2}$
Xylene	DPPP-10	*p, m, o*	80	1.07	1.12	1.33	1.05	1.19
	DPPP-20			1.15	1.21	1.45	1.05	1.20
	DPPP-25			1.25	1.31	1.59	1.05	1.21
Cresols	DPPP-10	*o, m, p*	120	1.13	1.29	1.47	1.14	1.14
	DPPP-20			1.13	1.29	1.49	1.14	1.15
	DPPP-25			1.14	1.30	1.51	1.14	1.16
Nitrotoluene	DPPP-10	*o, m, p*	160	0.73	0.88	0.97	1.20	1.10
	DPPP-20			0.89	0.91	0.99	1.03	1.09
	DPPP-25			0.69	0.84	0.94	1.22	1.12
Nitroaniline	DPPP-10	*o, m, p*	200	0.75	0.98	1.52	1.31	1.55
	DPPP-20			0.75	1.01	1.57	1.35	1.55
	DPPP-25			0.76	1.03	1.70	1.36	1.65

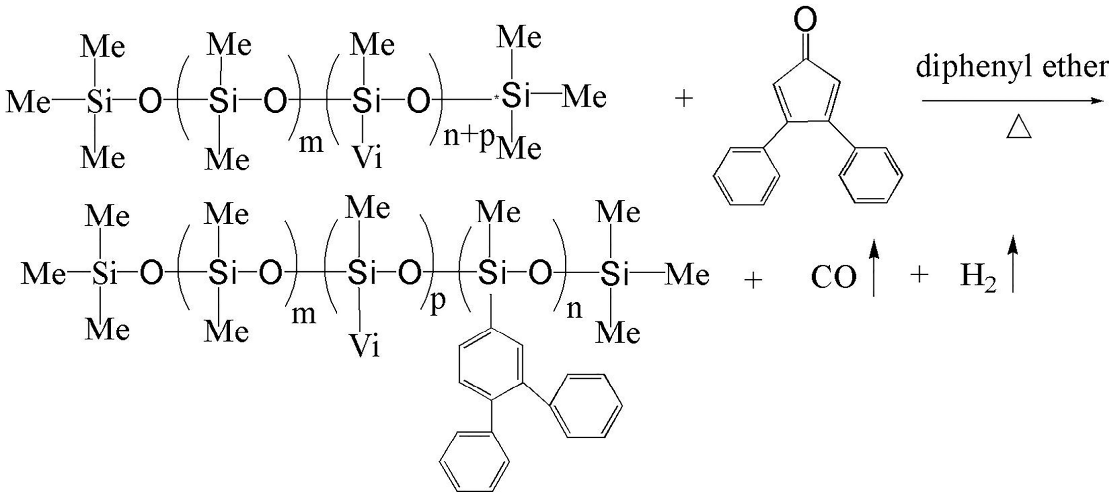

Fig. 1. Synthetic scheme of methyl diphenyl-phenyl polysiloxane.

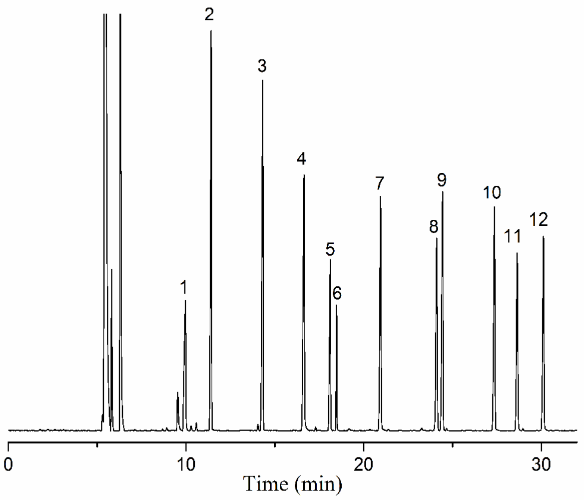

Fig. 2. Chromatogram of Grob test mixtures on the DPPP-25 column. Column: DPPP-25, 0.31 µm, 30 m × 0.25 mm (ID). Condition: 10 cm/s nitrogen linear velocity; 50 ºC to 170 ºC at 4 ºC min^{-1}. Peaks: 1. 2,3-butanediol; 2. n-decane; 3. n-undecane; 4. 1-octanol; 5. nonanal; 6. 2-ethylhexanoic acid; 7. 2,6-dimethylphenol; 8. 2,6-dimethylaniline; 9. methyl decanoate; 10. dicyclohexyl amine; 11. methyl undecanoate; 12. Methyl dodecanoate.

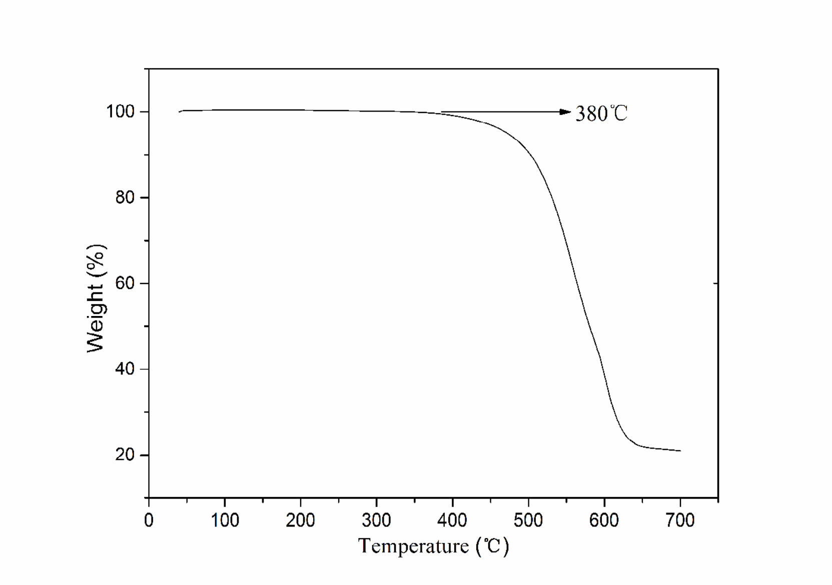

Fig. 3. TGA curve for the DPPP-25 stationary phase.

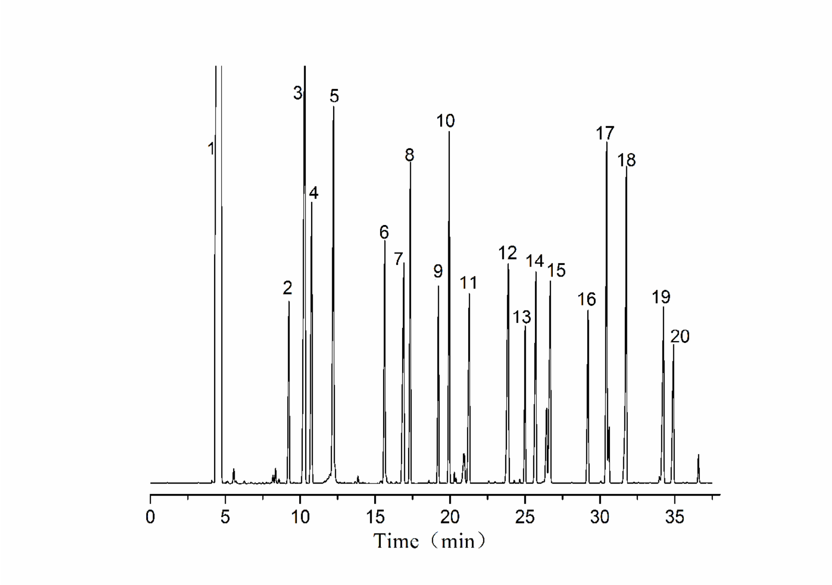

Fig. 4. Chromatogram of substituted benzenes on the DPPP-25 column. Injection and detection temperatures: 260 ºC. Temperature program: 40 ºC kept for 5 min, then from 40 ºC to 240 ºC at 5 ºC /min. Condition: 13.5 cm/s nitrogen linear velocity. Peaks: 1. benzene; 2. toluene; 3. chlorobenzene; 4. ethylbenzene; 5. *m*-xylene; 6. *p*-methylchlorobenzene; 7. 1,2,4-trimethylbenzene; 8. 1,3-dichloro- benzene; 9. butylbenzene; 10. nitrobenzene; 11. *o*-methylnitrobenzene; 12. *o*-ethylnitrobenzene; 13. 1,4-dibromobenzene; 14. *p*-methylnitrobenzene; 15. *p*-nitrochlorobenzene; 16. *p*-nitrobromobenzene; 17. biphenyl; 18. diphenylmethane; 19. 1-methyl-2,4-dinitrobenznen; 20. 1-chloro-2,4-dinitrobenzene.

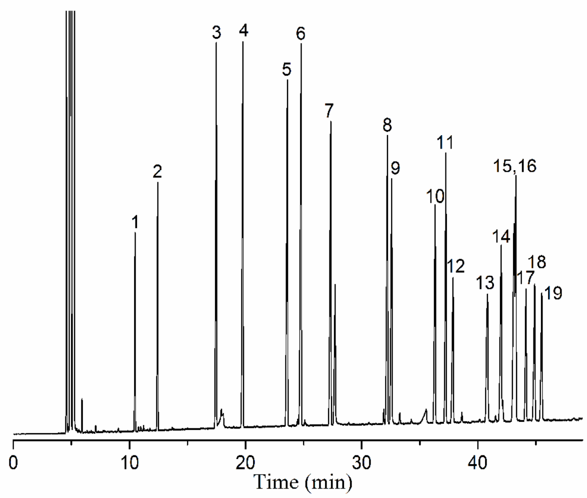

Fig. 5. Separation of polycyclic aromatic hydrocarbons on the DPPP-25 column. Injection and detection temperatures: 360 ºC. Temperature program: from 70 ºC to 320 ºC at 5 ºC/min. Condition: 13.5 cm/s nitrogen linear velocity. Peaks: 1. decahydronaphthalene; 2. tetralin; 3. naphthalene; 4. 2-methylnaphthalene; 5. 1-methylnaphthalene; 6. biphenyl; 7. 8-hydroxyquinoline; 8. dihydroacenaphthylene; 9. naphthyl ethyl ether; 10. α-nitronaphthalene; 11. dibenzyl ether; 12. phenanthrenequinone; 13. fluorenone; 14. phenanthrene; 15. philippines; 16. 4-nitrobiphenyl; 17. *β*-naphthol quinoline; 18. 1,8-dihydroxy anthraquinone; 19. pyrene**.**