ELSEVIER

Journal of Chromatography A, 932 (2001) 97–105

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Liquid crystalline polysiloxane polymer as stationary phase in gas chromatography capillary column for the separation of dioxin/furan compounds

Guo-Ping Chang-Chien[a,*], Wei-Shan Lee[a], Jin-Lian Tsai[b], Shwu-Huney Jeng[b]

[a]*Department of Chemical Engineering and Super Micro Mass Research and Technology Center, Cheng-Shiu Institute of Technology, 840 Cheng-Ching Road, Kaohsiung 833, Taiwan*

[b]*Graduate Institute of Occupation Safety and Health, Kaohsiung Medical University, Kaohsiung 833, Taiwan*

Received 16 November 2000; received in revised form 22 June 2001; accepted 16 August 2001

Abstract

A side-chain liquid crystalline polysiloxane polymer (PS3DBDE1) with high purity and high isotropic transition temperature served as a stationary phase in an attempt to chromatographize the dioxin/furan compounds. The polymer was coated on the inner surface of a 0.25 mm I.D. capillary column by using the static coating method, forming a film with a thickness of $d_f \approx 0.25$ μm. A commercial standard solution (US EPA 1613 standard solution 1613CS4) containing polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) was used to test the chromatographic behavior of the laboratory-made capillary column. Two commercial capillary columns HP-5MS (Hewlett-Packard) and RTX-5MS (RTX) were chosen to compare their chromatographic behavior. The results show that by the use of PS3DBDE1 the isomeric pair compounds 1,2,3,4-TeCDD vs. 2,3,7,8-TeCDD and 1,2,3,4,7,8-HxCDD vs. 1,2,3,6,7,8-HxCDD and the same substituted-chlorine number compounds 1,2,3,4,6,7,8-HpCDF vs. 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8,9-OCDD vs. 1,2,3,4,6,7,8,9-OCDF had higher resolution than HP-5MS and RTX-5MS as suggested by the column makers.

Keywords: Stationary phases, GC; Polysiloxanes; Dioxin; Furan

1. Introduction

Applications of side-chain liquid crystalline polymers (SCLCPs) have received much attention recently [1–5]. Applications such as uses in stationary phases for high-resolution gas chromatography (GC) have been reported [6–12]. A significant advancement in this field was achieved by grafting mesomorphic monomers onto a stable polysiloxane polymer. It has generally been thought that nematic phases can be resolved better than smectic phases in GC due to greater diffusion in the former, and thus, show higher efficiency. Two new and highly pure all-hydrocarbon side-chain liquid crystalline polysiloxane polymers were coated on the inner surface of the GC–MS capillary column as a stationary phase. It showed better resolution for PAH (polynuclear aromatic hydrocarbon) isomeric compounds than the commercial HP-5 column [13].

Polychlorinated dibenzo-*p*-dioxins (PCDDs), poly-

*Corresponding author. Tel.: +886-7-731-0606 ext. 305; fax: +866-7-731-4090.

E-mail address: guoping@cc.csit.edu.tw (G.-P. Chang-Chien).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01213-4

chlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), a class of highly stable lipophilic aromatic chemicals, have been either widely used in industry (PCBs) or found as by-products of industrial chemical preparations (PCDDs and PCDFs) and of combustion processes (PCDDs, PCDFs, and PCBs). Several epidemiologic and toxicological studies have suggested an association between 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TeCDD), or its family compounds and the diseases such as soft-tissue sarcoma, Hodgkin's disease, non-Hodgkin's lymphoma, stomach cancer, nosal cancer, and liver cancer [14–18].

The analytical method developed for investigation was required to meet six criteria: (1) to permit determinations of the majority of these compounds, especially those possessing more than three chlorine substituents; (2) to permit isomer-specific determinations of the most toxic or otherwise important components; (3) to provide a lower limit of detection for individual components of between 1 and 5 parts per trillion (pptr) in a variety of environmental samples; (4) to generate data with an acceptable and adequately defined level of accuracy and precision; (5) to exhibit a very low and well-defined susceptibility to interference and false-positive determinations; and (6) to minimize analyst's time requirements and to permit analyses of large numbers of samples [19].

In the analysis of pollutants, the choice of the sensitivity of the instrument is mostly based on species and concentrations of the pollutants. However, the resolution of a capillary column is also considered an important factor in this respect. The material coated on the inner surface of the capillary column determines its chromatographic behavior. Sometimes a specific column is adopted to analyze the interfering ingredient and the authentic sample is thus obtained (e.g., J&W Scientific DB-225 column) [20].

Riehle et al. [23] using a smectic liquid crystalline silicone phase to separate the PCDD/PCDF congerer compounds reported a unique selectivity for the separation of 2,3,7,8-TeCDF from all the other tetrachlorodibenzofurans. In this study, a new side-chain liquid crystalline polysiloxane polymer PS3DBDE1 as a stationary phase in a capillary column was installed in a GC–MS system to test the chromatographic behavior and compare selectivity for dioxin compounds with the commercial capillary columns HP-5MS and RTX-5MS.

Table 1
The mesophase transition temperature and mesophase type of the liquid crystal monomer MS3DBDE1 and polymer PS3DBDE1

Monomer	
Heating	K 151.29 N 230.32 I
Cooling	I 219.5 N 108.35 K
Polymer	
Heating	K 122.34, 133.73, 142.46 S 215.87 N 270.27 I
Cooling	I 262.80 N 204.82 S 128.84, 108.54 K

K: Crystalline; S: smectic mesophase; N: nematic mesophase; I: isotropic phase.

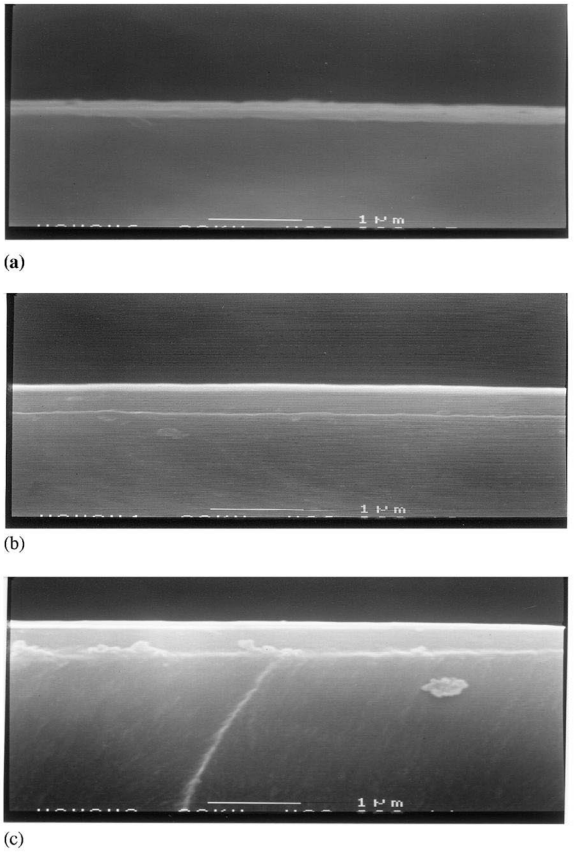

Fig. 1. Scanning electron micrography of the cross-sectional view of the (a) HP-5MS, (b) RTX-5MS, and (c) PS3DBDE1 columns (×20 000).

2. Experimental

2.1. Materials

The stationary phase material PS3DBDE1 used in this study is a liquid crystalline polysiloxane polymer, which shows both smectic and nematic mesophase. The synthesis procedures of the monomer and polymer were published previously [21]. The mesophase type and transition temperatures are listed in Table 1. The polysiloxane polymer has an average molecular mass of 11 000 with a polydispersity of 2.8 measured by gel permeation chromatography (GPC). An undeactivated fused-silica capillary column (2.5 mm I.D.) was purchased from J&W Scientific. The material of the test resolution standard solution (1613CS4) was purchased from Wellington (Guelph, Canada).

2.2. Capillary column preparation

The capillary column was washed with 10 ml methylene chloride before coating and then was purged by nitrogen gas for 1 h. The stationary phase,

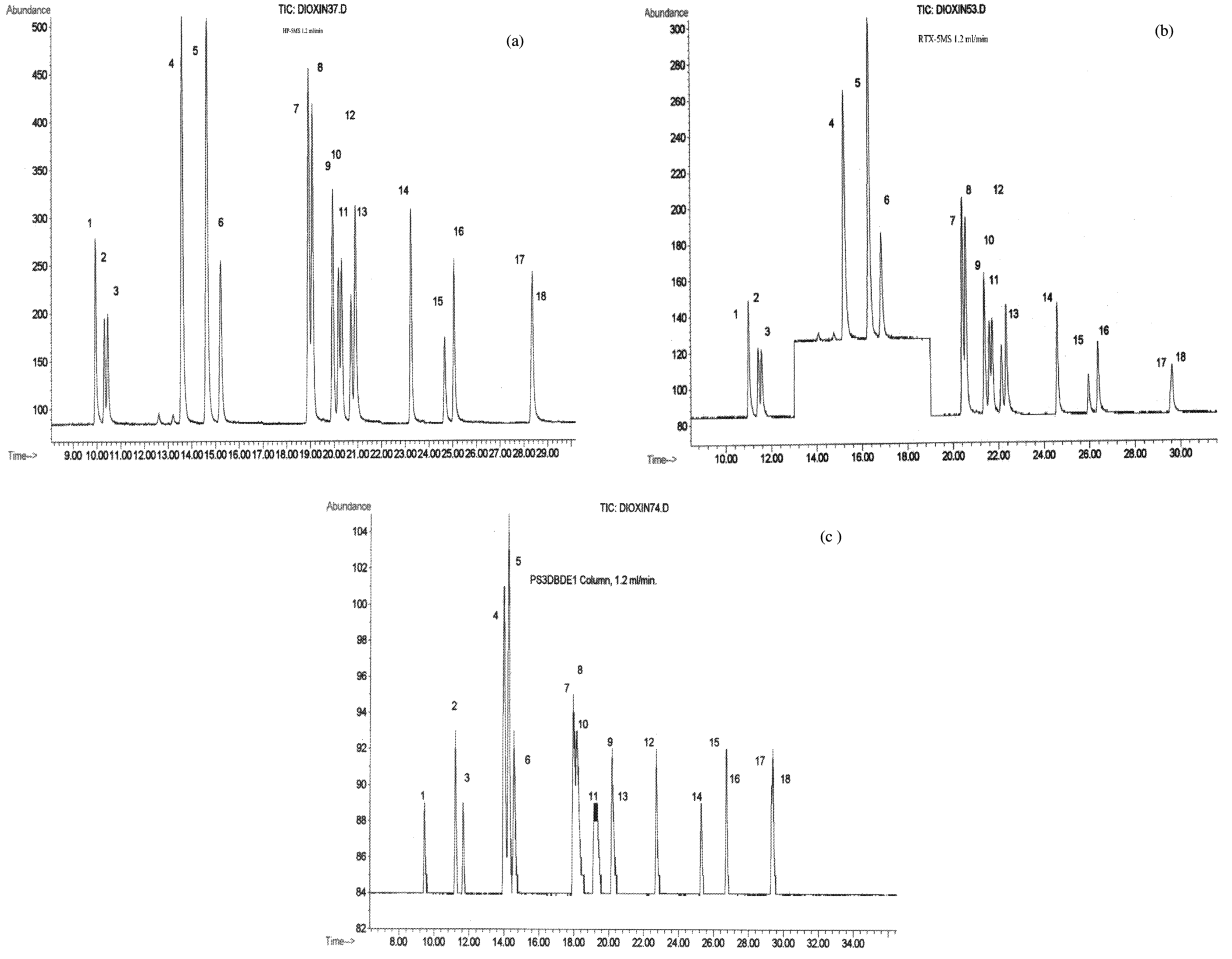

Fig. 2. Chromatograms of 1613CS4 standard solution (a) HP-5MS column, temperature programmed from 150 to 225°C at 15°C/min for 10 min and to 290°C at 4°C/min; splitless injection. (b) RTX-5MS column, temperature programmed from 150 to 225°C at 15°C/min for 10 min and to 290°C at 4°C/min; splitless injection. (c) PS3DBDE1 column, temperature programmed from 150 to 210°C at 10°C/min for 10 min and to 240°C at 2°C/min; splitless injection.

39.2 mg of polysiloxane polymer PS3DBDE1, was dissolved in 10 ml methylene chloride, degassed by ultrasonic before use. The polymer solution was filtered to remove the undissolved part in the polymer with a syringe filter (PTFE, pore size 0.2 μm). The filtered solution was placed in a screw cap septum bottle and was forced through the capillary column by nitrogen gas pressure. After the polymer solution reached the other end of the capillary column, it was sealed by being put in the glass tube containing gum. The tube was then dipped in the −20°C bath to freeze the gum. The capillary column was put in a controllable temperature bath. The solvent was evaporated by vacuum. So far the static coating was completed. The sealed end with gum was then cut off. After that, cross-linking was performed in a septum bottle by bubbling of vapor phase azo-*tert*.-butane (Lancaster, UK) with nitrogen as carrier gas at room temperature for 30 min and at a flow-rate of 2 ml/min. Both ends of the column were then sealed using the melting PET polymer. The column was heated from 50 to 140°C at 20°C/

Table 2
The dioxin/furan compounds in the 1613CS4 standard solution and the monitoring ion in the SIM mode for the GC–MS experiment

No.	Compound	Monitoring ions		Concentration (ng/ml)	Peak assignment
		First	Second		
1	2,3,7,8-TeCDF	304	305	40	
2	1,2,3,7,8-PeCDF	340	341	200	Peak 4
3	2,3,4,7,8-PeCDF	340	341	200	Peak 5
4	1,2,3,4,7,8-HxCDF	373	376	200	Peak 7
5	1,2,3,6,7,8-HxCDF	373	376	200	Peak 8
6	2,3,4,6,7,8-HxCDF	373	376	200	Peak 9
7	1,2,3,7,8,9-HxCDF	373	376	200	Peak 13
8	1,2,3,4,6,7,8-HpCDF	408	410	200	Peak 14
9	1,2,3,4,7,8,9-HpCDF	408	410	200	Peak 16
10	OCDF	441	443	400	Peak 18
11	2,3,7,8-TeCDD	320	322	40	
12	1,2,3,7,8-PeCDD	356	359	200	Peak 6
13	1,2,3,4,7,8-HxCDD	390	392	200	Peak 10
14	1,2,3,6,7,8-HxCDD	390	392	200	Peak 11
15	1,2,3,7,8,9-HxCDD	390	392	200	Peak 12
16	1,2,3,4,6,7,8-HpCDD	424	426	200	Peak 15
17	OCDD	458	460	400	Peak 17
(Labelled compounds, LCS)					
18	$^{13}C_{12}$-2,3,7,8-TeCDF	316	319	100	Peak 1
19	$^{13}C_{12}$-1,2,3,7,8-PeCDF	352	354	100	
20	$^{13}C_{12}$-2,3,4,7,8-PeCDF	352	354	100	
21	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	384	386	100	
22	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	384	386	100	
23	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	384	386	100	
24	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	384	386	100	
25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	418	420	100	
26	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	418	420	100	
27	$^{13}C_{12}$-2,3,7,8-TeCDD	332	334	100	Peak 2
28	$^{13}C_{12}$-1,2,3,7,8-PeCDD	368	370	100	
29	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	402	404	100	
30	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402	404	100	
31	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	436	438	100	
32	$^{13}C_{12}$-OCDD	470	472	200	
(cleanup standard solution, CSS)					
33	$^{37}Cl_4$-2,3,7,8-TeCDD	328		40	
(internal standards solution, ISS)					
34	$^{13}C_{12}$-1,2,3,4-TeCDD	332	334	100	Peak 3
35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402	404	100	

min and maintained at 140°C for 1 h. Both ends of the column were reopened, rinsed with 10 ml methylene dichloride with nitrogen gas, and then dried with pure nitrogen. Finally, the column was installed on a gas chromatography apparatus and conditioned at an initial temperature 150°C, and increased at a rate 1°C/min to 280°C, which was maintained for 4 h at a constant flow-rate of 1.2 ml/min nitrogen gas. The column prepared for chromatogram tests was 30 m long with an internal diameter of 0.25 mm. The thickness of the coating film was approximately 0.25 μm measured by scanning electron microscopy (SEM).

2.3. Column evaluation

A Hewlett-Packard Model 5890 series II gas chromatograph equipped with a 5972 series mass-selective detector and a 6890 series injector with an autosampler controller were used for column evaluation. Helium was used as the carrier gas.

3. Results and discussion

The thickness of the gum film was initially estimated by the equation of Bouche and Verzele [22]. Furthermore, the thickness of the coating film was further confirmed by SEM. The SEM pictures are shown in Fig. 1a–c. The measured thickness obtained from SEM is about 0.25 μm, close to the calculated thickness by the equation of Bouche and Verzele. The surface of the coating film of the PS3DBDE1 column is visually rougher than that of the HP-5MS and RTX-5MS columns. As we know, the column chromatography behavior is dependent on the flow-rate of carrier gas, film thickness, and chemical properties of the coating film. In this study, we test the column chromatographic behavior of the above three columns with a variety of flow-rates, 0.8, 1.2, 1.5, 2.0, and 4.0 ml/min. Fig. 2a–c, respectively, show the GC–MS chromatograms in the selected ion monitoring (SIM) mode for the HP-5MS, RTX-5MS, and PS3DBDE1 columns. The peak numbers are labeled in Fig. 2a–c. The monitoring ions are listed in Table 2. Group 1: peaks 1–3. Group 2: peaks 4–6. Group 3: peaks 7~13. Group 4: peaks 14~16, and group 5: peaks 17 and 18. Comparing Fig. 2a with Fig. 2b, we find that their characteristics and retention times of the peaks are close. Both of them are likely to have the same chemical properties. Inspecting Fig. 2a or Fig. 2b, we find peaks 1, 4, 5, 6, 9, 14, 15, and 16 show better resolution, while peaks 2 and 3, peaks 7 and 8, peaks 10 and 11, peaks 12 and 13, and peaks 17 and 18, overlap each other.

Table 3
The theoretical plates at various carrier gas flow-rate, 0.8, 1.2, 1.5, 2.0, and 4.0 ml/min, for the HP-5MS column

Compound	Theoretical plates (N)				
	0.8 ml/min	1.2 ml/min	1.5 ml/min	2.0 ml/min	4.0 ml/min
2,3,7,8-TeCDF (peak 1)	112 598	129 803	156 909	158 558	151 748
2,3,7,8-TeCDD (peak 2)	138 309	139 506	168 407	169 816	146 833
1,2,3,7,8-PeCDF (peak 4)	138 075	160 015	177 951	145 010	92 070
2,3,4,7,8-PeCDF (peak 5)	157 435	146 723	154 367	167 054	104 726
1,2,3,4,7,8-HxCDF (peak 7)	359 530	310 472	195 149	163 642	62 010
1,2,3,4,7,8-HxCDD (peak 10)	421 058	353 143	301 726	192 900	283 945
1,2,3,4,6,7,8-HpCDF (peak 15)	634 156	525 167	487 473	387 743	–
1,2,3,4,6,7,8,9-OCDD (peak 17)	817 644	694 877	651 508	542 247	305 285

Table 4
The theoretical plates at various carrier gas flow-rate, 0.8, 1.2, 1.5, 2.0, and 4.0 ml/min, for the RTX-5MS column

Compound	Theoretical plates (N)				
	0.8 ml/min	1.2 ml/min	1.5 ml/min	2.0 ml/min	4.0 ml/min
2,3,7,8-TeCDF (peak 1)	89 576	119 388	161 195	133 219	155 675
2,3,7,8-TeCDD (peak 2)	96 894	113 093	205 574	142 841	166 084
1,2,3,7,8-PeCDF (peak 4)	117 255	158 579	434 728	137 769	111 585
2,3,4,7,8-PeCDF (peak 5)	188 753	182 329	504 387	159 074	111 180
1,2,3,4,7,8-HxCDF (peak 7)	384 400	319 862	324 402	220 078	34 509
1,2,3,4,7,8-HxCDD (peak 10)	305 181	319 392	357 950	253 148	94 795
1,2,3,4,6,7,8-HpCDF (peak 15)	868 290	584 789	542 804	467 512	198 454
1,2,3,4,6,7,8,9-OCDD (peak 17)	611 897	598 171	562 694	573 127	376 057

An examination of the chromatogram of column PS3DBDE1 shows a different elution sequence for group 3 (peaks 7 to 13). The column has better resolution for peaks 1–3 in group 1 and peaks 11 and 12 in group 3. The others show lower resolution than columns HP-5MS and RTX-5MS. Riehle et al. [23] studying selectivity of two pairs 2,3,7,8-TeCDF and other tetrachlorodibenzofurans, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF in the same smectic mesophase capillary column with different molecular structure showed different elution sequences. Column selectivity is examined with a series of smectic liquid crystalline columns. It is also compared with methyl and C_{18} polysiloxane columns for the separation of PAH isomers. Sander et al. suggested that shape factors contribute significantly to retention time and chromatographic behavior is more complicated than predicted by the ratio of the length to width of the molecule (L/B) alone [24]. The selectivity ratio for tetraphenylmethane and *p*-terphenyl with different L/B values shows a tendency of column sensitivity, with a change in elution order occurring between ordered liquid crystalline column and non-ordered polysiloxane column. Investigating the molecular structure for the PCDDs/PCDFs, the difference in the L/B value for the PCDDs/PCDFs is not so obvious as in tetraphenylmethane and *p*-terphenyl studied by Sander et al. [24].

The following compound pairs, peak 1 vs. peak 2, peak 2 vs. peak 3, peak 4 vs. peak 5, peak 5 vs. peak 6, peak 7 vs. peak 8, peak 10 vs. peak 11, peak 15 vs. peak 16, and peak 17 vs. peak 18, were chosen to calculate the theoretical plates (N) and resolution of the three columns. Tables 3–5, respectively, show the theoretical plates at various carrier flow-rates,

Table 5
The theoretical plates at various carrier gas flow-rate, 0.8 and 1.2 ml/min, for the PS3DBDE1 column

Compound	Theoretical plates (N)	
	0.8 ml/min	1.2 ml/min
2,3,7,8-TeCDF (peak 1)	81 184	77 372
2,3,7,8-TeCDD (peak 2)	89 905	108 682
1,2,3,7,8-PeCDF (peak 4)	52 173	55 173
2,3,4,7,8-PeCDF (peak 5)	71 287	77 974
1,2,3,4,7,8-HxCDF (peak 7)	52 173	47 142
1,2,3,4,7,8-HxCDD (peak 10)	61 652	22 854
1,2,3,4,6,7,8-HpCDF (peak 15)	–	388 223
1,2,3,4,6,7,8,9-OCDD (peak 17)	–	588 377

0.8, 1.2, 1.5, 2.0, and 4.0 ml/min, for the HP-5MS, RTX-5MS, and PS3DBDE1 columns.

Examining Tables 3 and 4 show the theoretical plates range from 89 000 to 870 000, dependent on the carrier flow-rates and the compound pairs. The data in Table 5 for column PS3DBDE1 show the theoretical plates range from 22 000 to 588 000. It is also related to the carrier flow-rates and compound pairs. On the whole, the theoretical plates for the PS3DBDE1 column are smaller than for the HP-5MS and RTX-5MS columns. It indicates that the plate efficiency of column PS3DBDE1 is lower than the commercial columns. Apparently, the diffusion separation mechanisms for the solutes in a liquid crystalline stationary phase should have a greater influence on plate efficiency than other separation factors, such as vapor pressure and polarity. Fig. 3a–h, respectively, show the relationship of the resolution with the carrier flow-rates for peak 1 vs. peak 2, peak 2 vs. peak 3, peak 4 vs. peak 5, peak 5 vs. peak 6, peak 7 vs. peak 8, peak 10 vs. peak 11, peak 15 vs. peak 16, and peak 17 vs. peak 18. In Fig. 3a–h, the resolutions for peak 1 vs. peak 2, peak 2 vs. peak 3, peak 10 vs. peak 11, and peak 17 vs. peak 18 are obtained by using the PS3DBDE1 column, which is better than the resolution of those peaks using the HP-5MS and RTX-5MS columns. It is worth noting that the elution time of peak 12 is far

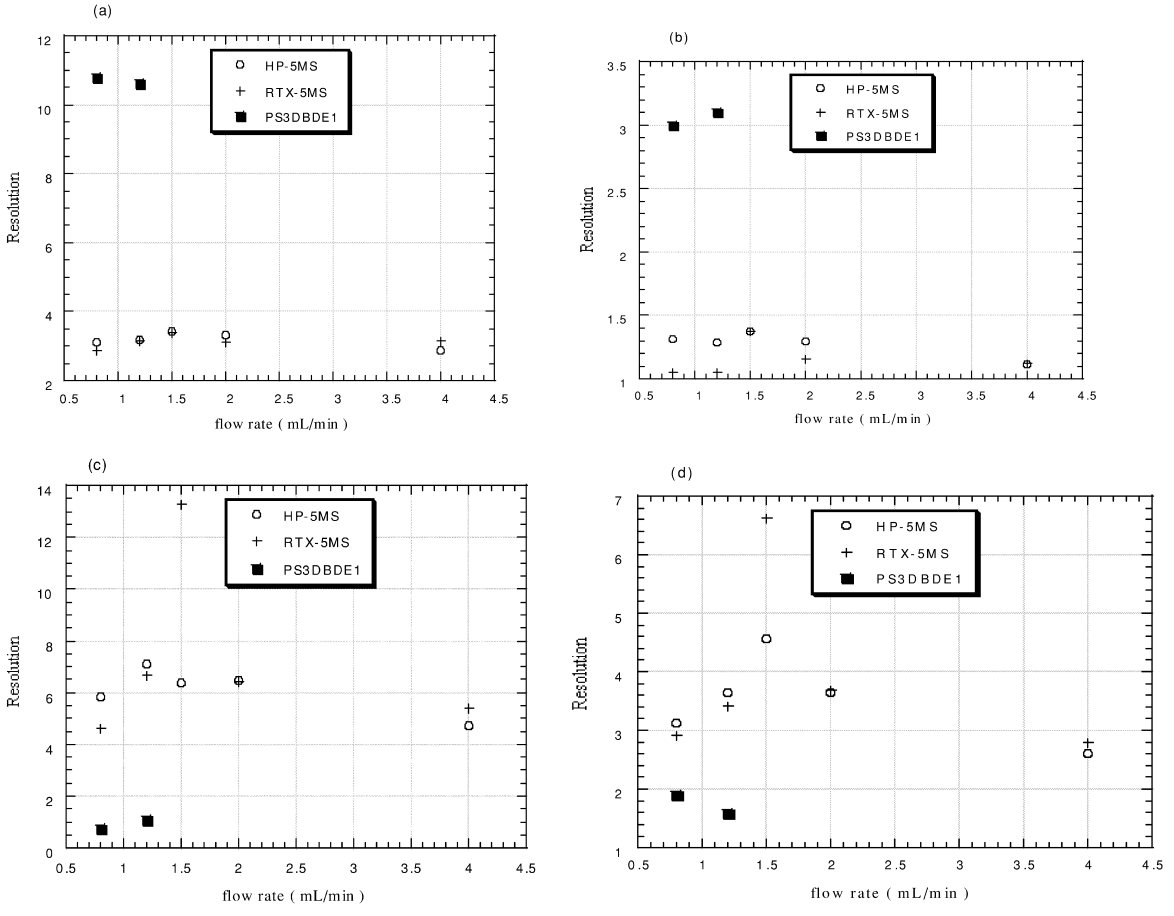

Fig. 3. The relationship of the resolution with the carrier gas flow-rate for (a) peak 1 vs. peak 2, (b) peak 2 vs. peak 3, (c) peak 4 vs. peak 5, (d) peak 5 vs. peak 6, (e) peak 7 vs. peak 8, (f) peak 10 vs. peak 11, (g) peak 15 vs. peak 16, and (h) peak 17 vs. peak 18 for HP-5MS, RTX-5MS, and PS3DBDE1 columns.

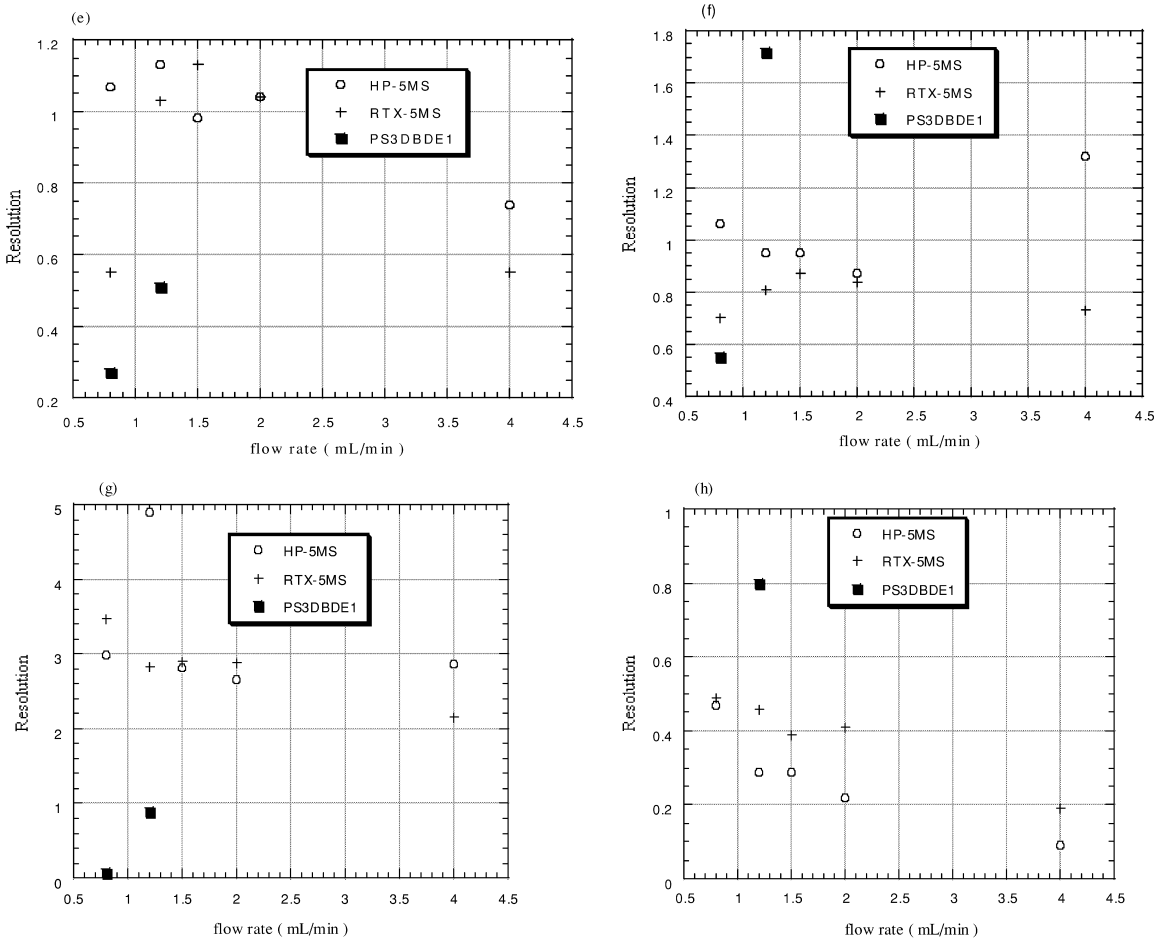

Fig. 3. (*continued*)

from those peaks of group 3, although we do not calculate the resolution of peak 12.

An experienced researcher believes that it is crucial to choose an appropriate column when analyzing some special species of environmental matrixes. In the US Environmental Protection Agency (EPA) 23 and 1613 methods, columns DB-5, DB-5MS, HP-5MS, and RTX-5MS are often suggested for analyzing dioxin/furan compounds. All these columns display pretty good resolution and repeatability except for the native compound 2,3,7,8-TeCDF in the real sample (e.g., fly ash or incineration samples). Native 2,3,7,8-TeCDF is not completely resoluted and it overlaps the other compounds in the GC–MS chromatogram, despite the use of high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS). The toxicity equivalent factor for 2,3,7,8-TeCDF (2,3,7,8-tetra chlorine dibenzo-*p*-furan) is 1.0, suggested by the World Heath Organization. The value is the same as that of 2,3,7,8-TeCDD (tetra chlorine dibenzo-*p*-dioxin), the most toxic compound. It results in an overestimation of the toxic equivalency factor (TEQ) value (TEQ-ng/g-sample or TEQ-ng/NM^3) caused by overlapping peaks. Therefore, the US EPA 23 and 1613 methods suggest that the DB-225 column replace the DB-5 or HP-5 columns to analyze the 2,3,7,8-TeCDF compound in environmental matrices. Some recent research data in our laboratory show that the analysis concentration of 2,3,7,8-TeCDF

with the DB-5 column is about six times as much as the concentration obtained by the DB-225 column. The PS3DBDE1 column used in real environmental matrices (incinerator stack samples and ambient samples) will be researched in the future. The resolution of the 2,3,7,8-TeCDF compound will be compared with that for the DB-225 column (J&W Scientific).

Acknowledgements

This work was kindly supported by the National Science Council of Taiwan (NSC-89-2216-E-230-001).

References

[1] K.M. Blackwood, Science 273 (No. 5277) (1996) 909.
[2] H. Andersson, F. Sahlen, M. Trollsas, U.W. Gedde, A. Hult, J. Macromol. Sci. Pure Appl. Chem. A3310 (1996) 1427.
[3] K. Nakamura, H. Kikuchi, T. Kajiyama, Polym. J. 26 (No. 9) (1994) 1090.
[4] J.C. Hwang, H. Kikuchi, T. Kajiyama, Polym. J. 27 (No. 3) (1995) 292.
[5] J.C. Hwang, Y. Fuwa, H. Moritake, H. Gu, M. Ozaki, K. Yoshino, Jpn. J. Appl. Phys. Part 2: Lett. 34 (No. 5A) (1995) L560.
[6] B.A. Jones, J.S. Bradshaw, M. Nishioka, M.L. Lee, J. Org. Chem. 49 (1984) 4947.
[7] K.E. Markides, M. Nishioka, B.J. Tarbet, J.S. Bradshaw, M.L. Lee, Anal. Chem. 57 (1985) 1296.
[8] K. Gorczynska, T. Kreczmer, D. Ciecierskastoklosa, A. Utnik, J. Chromatogr. 509 (1990) 53.
[9] R. Fu, P. Jing, J. Gu, Z. Huang, Y. Chen, Anal. Chem. 65 (1993) 2131.
[10] J. Mazur, Z. Witkiewicz, R. Dabrowski, J. Chromatogr. 600 (1992) 123.
[11] L. Sojak, I. Ostrovsky, R. Kubinec, G. Kraus, A. Kraus, J. Chromatogr. 609 (1992) 283.
[12] J.T. Betts, J. Chromatogr. 588 (1991) 231.
[13] W.-S. Lee, G.-P. Chang-Chien, Anal. Chem. 70 (1998) 4094.
[14] L. Hardell, A. Sandstrom, Br. J Cancer 39 (1979) 711.
[15] L. Hardell, No. Bengtsson, Br. J. Cancer 48 (1983) 217.
[16] L. Hardell, M. Eriksson, P. Lenner, E. Lundgren, Br. J. Cancer 43 (1981) 169.
[17] O. Axelson, L. Sundell, K. Andersson, C. Edling, C. Hogstegt, H. Kling, Scand. J. Work Environ. Health 6 (1980) 73.
[18] National Toxicology Program (NTP), Carcinogensis Boassay of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (CAS No. 1746-01-6) in Osborne–Mendel Rats and B6C3F1 Mice (Gavage Study), DHHS Publication No. (NIH) 82-1765, Government Printing Office, Washington, DC, 1982.
[19] L.M. Smith, D.L. Stalling, J.L. Johnson, Anal. Chem. 56 (1984) 1830.
[20] Tetra- Through Octa-Chlorinated Dioxins and Furans By Isotope Dilution HRGC/HRMS, US Environmental Protection Agency Office of Water Engineering and Analysis Division, 1994.
[21] G.P. Chang-Chien, J.F. Kuo, J. Appl. Polym. Sci. 57 (1995) 1183.
[22] J. Bouche, M. Verzele, J. Gas Chromatogr. 6 (1968) 501.
[23] U. Riehle, J. Ehmann, M. Swerev, K. Ballschmiter, Fresenius Z. Anal. Chem. 331 (1988) 821.
[24] L.C. Sander, H. Schneider, S.A. Wise, C. Woolley, J. Microcol. Sep. 6 (No. 2) (1994) 115.