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Computer-assisted automatic peak recognition and result evaluation for analysis of chlorinated hydrocarbons in environmental samples

X.Y. Xue^a, Q. Zhang^a, X.M. Liang^{a,*}, K. Oxynos^b, A. Kettrup^b, P.C. Lu^a

^a*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 161 Zhongshan Road, Dalian 116011, PR China*

^b*GSF-Forschungszentrum für Umwelt und Gesundheit, Institut für Ökologische Chemie, Ingolstädter Landstrasse 1, D-85764 Neuherberg, Germany*

Abstract

A data manipulation method has been developed for automatic peak recognition and result evaluation in the analysis of organic chlorinated hydrocarbons with dual-column gas chromatography. Based on the retention times of two internal standards, pentachlorotoluene and decachlorobiphenyl, the retention times of chlorinated hydrocarbons can be calibrated automatically and accurately. It is very convenient to identify the peaks by comparing the retention times of samples with the calibrated retention times calculated from the relative retention indices of standards. Meanwhile, with a suggested two-step evaluation method the evaluation coefficients and the suitable quantitative results of each component can be automatically achieved for practical samples in an analytical system using two columns with different polarities and two internal standards. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Peak recognition; Automation; Environmental analysis; Organochlorine compounds; Pesticides; Polychlorinated biphenyls

1. Introduction

Chlorinated hydrocarbons (CHCs) play an important role as environmental contaminants [1–4]. Mainly in the past, they have been intensively used worldwide as effective insecticides (DDT, hexachlorocyclohexane (HCH) and related compounds) and as transformer oils (polychlorinated biphenyls, PCBs). Improper use and disposal of commercial CHC-containing materials have resulted in contamination of the environment including soil, water, marine life, etc. [5–9]. Although production of some CHCs has been drastically reduced or banned, they are still distributed all over the world due to their

high resistance to chemical transformation, low biological degradation and high accumulation factors in fatty tissues [10]. Therefore, much effort has been dedicated to developing analytical methods for their identification and quantification. Diverse GC methods for the determination of CHCs have been established [11–13]. Hale and Greaves published an excellent review of the analysis of persistent chlorinated hydrocarbons in tissues including sample preparation and instrumental systems [14]. Nevertheless, as samples from different sources are of different matrices, the determination is often seriously disturbed by matrix interference and errors are possibly caused during recognition and quantification. GC with electron-capture detection (ECD) on dual fused-silica capillary columns is an applicable method for the determination of CHCs [15,16]. Unquestionably, an efficient data manipulation meth-

*Corresponding author. Fax: +86-411-369-8905.

E-mail address: liangxm@mail.dlptt.ln.cn (X.M. Liang).

od would be beneficial to the analysis of CHCs with the system mentioned above [16].

We describe a data manipulation method which is developed for automatic peak recognition and the resulting evaluation in the analysis of organic chlorinated hydrocarbons with dual-column gas chromatography. Depending on the retention times of two internal standards, the calibrated retention times are calculated and used to recognize the components. Furthermore, suitable quantitative results of each component can also be obtained through evaluation of the four calculated concentrations based on two internal standards and on two columns.

2. Theory

In the analysis of CHCs, pentachlorotoluene (PCT) and decachlorobiphenyl (DCB) are used as the internal standards to calculate the concentrations of all related components. The retention times of these two compounds can be obtained very easily, and are thus used in the method to identify other CHCs according to the relative retention index, which has been practically adopted in the peak identification of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in environmental samples [17,18].

For each CHC component, the relative retention index can be calculated according to the retention data from the standard analytical chromatogram as follows:

$$P_i = (t_i - t_{\text{PCT}}) / (t_{\text{DCB}} - t_{\text{PCT}}) \quad (1)$$

where P_i is the relative retention index of the i th component, which is a constant for different samples in the same chromatographic system, and t_i , t_{PCT} and t_{DCB} are the retention times of the i th component, the first internal standard PCT and the second internal standard DCB, respectively.

After running the analysis of standard mixtures, the P_i values of each component can be calculated easily using Eq. (1). For actual work, the two internal standards must be correctly recognized, then the calibrated retention times of other components can be calculated with:

$$t_{i(\text{calib.})} = t'_{\text{PCT}} + P_i(t'_{\text{DCB}} - t'_{\text{PCT}}) \quad (2)$$

where $t_{i(\text{calib.})}$ is the calibrated retention time of the i th component, and t'_{PCT} and t'_{DCB} are the retention times of PCT and DCB in practical samples, respectively.

In addition, for each component, two concentrations can be calculated depending on two internal standards, PCT and DCB, on each column, and four calculated concentrations are thus obtained on two columns. The relative peak height ratio, the separation ratio and the relative deviation of half peak width are applied to evaluate these results and produce a reasonable outcome.

3. Experimental

The samples were prepared according to the “Standard operation procedures (SOPs)—analysis of chlorinated hydrocarbons in environmental samples” [16]. Abbreviations of the 21 chlorinated hydrocarbons mentioned in this paper are given in Table 1. All solvents (residue analysis grade) were purchased from Promochem (Wesel, Germany). All standards (purity >98%) were obtained from Dr Ehrenstorfer (Augsburg, Germany). Gas chromatographic experiments were performed on a Fisons HRGC MEGA 2 series capillary gas chromatograph (Fisons, Milan, Italy) with two electron-capture detectors. A 1- μ l sample was injected with a CTC A200s auto-sampler in splitless mode, and split into two fused-silica capillary columns (60 m \times 0.32 mm I.D.) coated with DB-1701 (column A) (Agilent J&W, Folsom, CA, USA) and DB-5 (column B) (Agilent J&W) simultaneously. H_2 was used as the carrier gas at 2 ml/min. The following temperature program was used: 60–120 °C at 8°/min, 120–260 °C at 5°/min and 260–280 °C at 10°/min and hold for 10 min. The software used was developed by our group based on the PC-800 Integrator (Waters, Milford, MA, USA). All data acquisition, peak recognition and evaluation of results were performed automatically with the software.

4. Results and discussion

4.1. Peak recognition

A standard sample was analyzed to calculate the

Table 1
Compounds used

No	Abbreviation	Name
1	PCBz	Pentachlorobenzene
2	PCT	Pentachlorotoluene
3	HCB	Hexachlorobenzene
4	α -HCH	α -Hexachlorocyclohexane
5	γ -HCH	γ -Hexachlorocyclohexane
7	HC	Heptachlor
8	Aldrin	Aldrin
10	OCS	Octachlorostyrene
11	β -HCH	β -Hexachlorocyclohexane
12	HE	Heptachlorepoide
14	4,4'-DDE	4,4'-Dichlorodiphenyldichloroethene
15	Dieldrin	Dieldrin
18	4,4'-DDT	4,4'-Dichlorodiphenyltrichloroethane
6,9,13,16,17,19	PCB-28, -52, -101, -153, -138, -180	Polychlorinated biphenyls
20	DCB	Polychlorinated biphenyls
21	DDD	4,4'-Dichlorodiphenyldichloroethane

relative retention index P_i of each component according to Eq. (1). The two internal standards, PCT and DCB, were identified in a practical sample for analysis using the classical time-window matching method, and the retention times of PCT and DCB were applied to calculate the calibrated retention times of each component with the obtained relative indices from the standard sample with Eq. (2). The retention times of components in the standard sample $t_R(\text{std})$, in the practical sample $t_R(\text{sm})$, and after calibration $t_R(\text{cal})$ on two columns are shown in Table 2. From Table 2 we can see that $t_R(\text{sm})$ values are closer to $t_R(\text{cal})$ than $t_R(\text{std})$. The average differences in retention times between the practical and standard samples are 0.0418 min for column A and 0.0244 min for column B. The biggest differences in retention times are 0.0533 min for A and 0.0300 for B. However, after calibration the average differences in retention times between the calibrated and the practical samples are found to be very small, i.e. 0.0079 min for column A and 0.0044 min for column B. The biggest differences in retention times are 0.0192 min for A and 0.0080 for B. Therefore it is obvious that $t_R(\text{cal})$ values are more reliable than $t_R(\text{std})$ values in computer-assisted automatic peak recognition.

The full chromatogram of a practical sample is shown in Fig. 1, and part of the full chromatogram before and after calibration is shown in Fig. 2. In Fig. 2, the solid and dotted identification lines lie at

the positions corresponding to $t_R(\text{cal})$ and $t_R(\text{std})$, respectively. As the time-window method is used to identify these peaks directly, the dotted identification lines depart from the peak top, which is liable to mis-recognition of neighboring peaks with similar retention times or big differences in peak size. But each of the solid identification lines pass through every peak top, which shows that using $t_R(\text{cal})$ can improve the accuracy of recognition.

4.2. Result evaluation

The results of CHC analysis were processed according to the two-step evaluation method, that is evaluating the matrix interference of internal standards and the separation status of each component on column A and B.

The first step is to evaluate the matrix interference of internal standards. Ideally, the relative peak height ratio $R = \frac{(H_{\text{DCB}}/H_{\text{PCT}})}{(H_{\text{DCB}}^0/H_{\text{PCT}}^0)}$ (H_{DCB} and H_{PCT} represent the peak heights of DCB and PCT in practical sample, respectively, and the superscript 0 denotes those in standard sample) equals 1 as the same amount of internal standards is added in practical sample as in standard sample. In practice, however, the R value obtained generally is not equal to 1 because of matrix interference. Thus, the R value can be regarded as a parameter for evaluating the matrix interference of internal standards. When the R value

Table 2
Comparison of the retention times before and after calibration

Compound	t_R (smp) (min)	t_R (cal) (min)	t_R (std) (min)	Error 1 (min)	Error 2 (min)
<i>Column A (DB-1701)</i>					
PCBz	9.7933	9.7871	9.8200	0.0062	0.0267
PCT	12.5667	12.5667	12.6000	0.0000	0.0333
HCB	13.1933	13.1933	13.2267	0.0000	0.0334
α -HCH	14.9900	14.9996	15.0333	0.0096	0.0433
γ -HCH	16.5467	16.5560	16.5900	0.0093	0.0433
PCB-28	17.0567	17.0759	17.1100	0.0192	0.0533
HC	17.2500	17.2559	17.2900	0.0059	0.0400
Aldrin	18.1433	18.1525	18.1867	0.0092	0.0434
PCB-52	18.4367	18.4424	18.4767	0.0057	0.0400
OCS	19.3333	19.3423	19.3767	0.0090	0.0434
β -HCH	19.8000	19.8155	19.8500	0.0155	0.0500
HE	21.0200	21.0320	21.0667	0.0120	0.0467
PCB-101	21.5733	21.5885	21.6233	0.0152	0.0500
4,4'-DDE	22.9433	22.9517	22.9867	0.0084	0.0434
Dieldrin	23.0667	23.0716	23.1067	0.0049	0.0400
PCB-153	24.6267	24.6347	24.6700	0.0080	0.0433
PCB-138	25.7700	25.7745	25.8100	0.0045	0.0400
4,4'-DDT	26.3033	26.3144	26.3500	0.0111	0.0467
PCB-180	28.1300	28.1341	28.1700	0.0041	0.0400
DCB	32.9433	32.9433	32.9800	0.0000	0.0367
<i>Column B (DB-5)</i>					
PCBz	14.5833	14.5774	14.6067	0.0059	0.0234
PCT	17.9967	17.9967	18.0233	0.0000	0.0266
α -HCH	18.4333	18.4304	18.4567	0.0029	0.0234
HCB	18.7400	18.7406	18.7667	0.0006	0.0267
β -HCH	19.5533	19.5579	19.5833	0.0046	0.0300
β -HCH	19.7967	19.7981	18.8233	0.0014	0.0266
PCB-28	22.2233	22.2300	22.2533	0.0067	0.0300
HC	22.7533	22.7538	22.7767	0.0005	0.0234
PCB-52	23.6433	23.6478	23.6700	0.0045	0.0267
Aldrin	24.1100	24.1114	24.1333	0.0014	0.0233
OCS	25.6633	25.6694	25.6900	0.0061	0.0267
HE	25.8900	25.8962	25.9167	0.0062	0.0267
PCB-101	27.0900	27.0972	27.1167	0.0072	0.0267
Dieldrin	28.1200	28.1280	28.1467	0.0080	0.0267
4,4'-DDE	28.2367	28.2414	28.2600	0.0047	0.0233
PCB-153	30.3567	30.3630	30.3800	0.0063	0.0233
4,4'-DDT	31.2233	31.2304	31.2467	0.0071	0.0234
PCB-138	31.3700	31.3771	31.3933	0.0071	0.0233
PCB-180	33.9000	33.9058	33.9200	0.0058	0.0200
DCB	39.3133	39.3133	39.3233	0.0000	0.0100

Error 1: $t_R(\text{cal}) - t_R(\text{smp})$; error 2: $t_R(\text{std}) - t_R(\text{smp})$. $t_R(\text{smp})$ and $t_R(\text{std})$ represent retention times of sample and standard, respectively. $t_R(\text{cal})$ represents retention time calibrated.

is larger than 1, the relative peak height of DCB in comparison to PCT is increased, which means DCB is disturbed more than PCT. If the R value is much larger than 1, PCT should be chosen as the only

effective internal standard, and the calculated concentrations based on PCT should be accepted. Otherwise, DCB should be selected as the only effective internal standard.

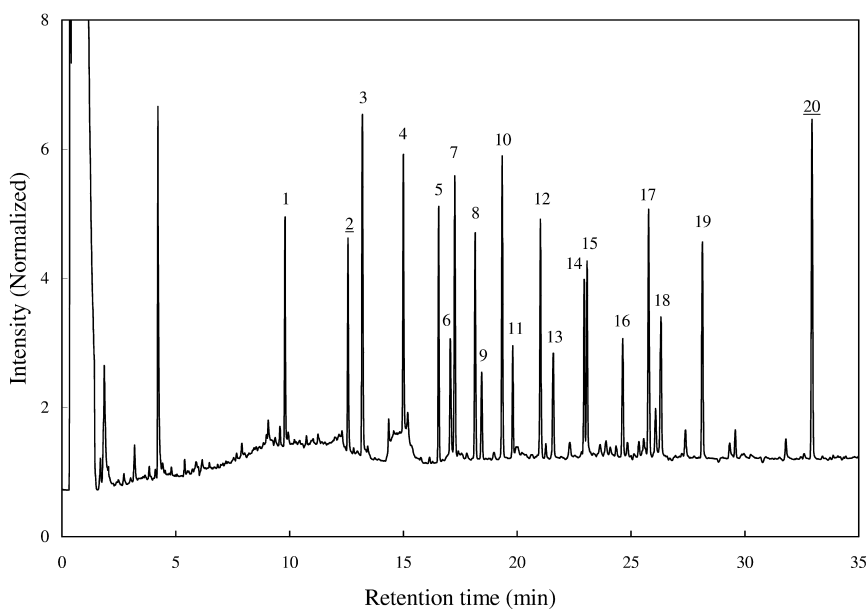


Fig. 1. Full chromatogram of a practical sample.

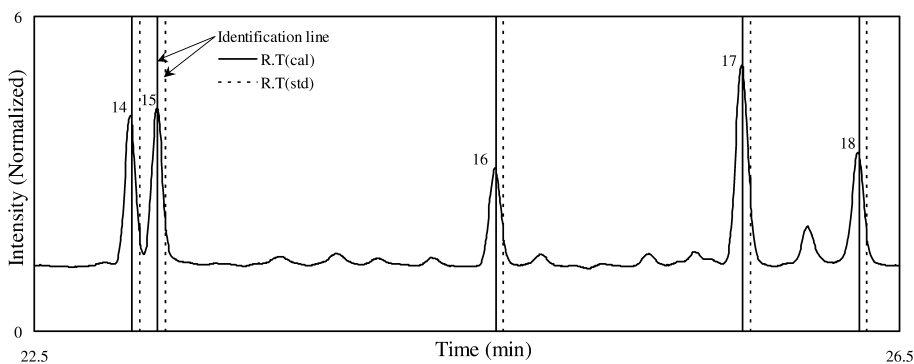


Fig. 2. A part of the full chromatogram before and after calibration.

The R values of DCB and PCT in three standard samples and one practical sample are listed in Table 3. For the three standard samples, the R values range from 0.95 to 1.05: this is thus considered as the

acceptable range of matrix interference of internal standards. For the practical sample, the R values on columns A and B are 0.91 and 0.84, respectively. Both are lower than 0.95 though the R value on

Table 3

Comparison of the relative peak height ratio of DCB to PCT in three standard samples (Std, Std1 and Std2) and one practical sample

Column	$H_{\text{DCB}}/H_{\text{PCT}}$				R		
	Std	Std1	Std2	Pract.	Std1	Std2	Pract.
A (DB-1701)	1.82	1.85	1.87	1.65	1.02	1.03	0.91
B (DB-5)	2.20	2.21	2.20	1.85	1.00	1.00	0.84

Table 4
Comparison of the half peak width and the separation ratio of all components in three standard samples

Comp.	$W_{1/2}$ (std) (min)	$W_{1/2}$ (std1) (min)	$W_{1/2}$ (std2) (min)	$Err_{1/2}$ (std1) (%)	$Err_{1/2}$ (std2) (%)	K_3 (std)	K_3 (std1)	K_3 (std2)
<i>Column A (DB-1701)</i>								
PCBz	2.59	2.57	2.59	0.77	0.00	1.00	1.00	0.98
PCT	2.97	3.01	2.96	1.35	0.34	1.00	1.00	0.99
HCB	3.23	3.33	3.25	3.10	0.62	1.00	1.00	1.00
α -HCH	2.84	2.82	2.76	0.70	2.82	1.00	1.00	1.00
γ -HCH	2.96	2.98	2.93	0.68	1.01	1.00	1.00	1.00
PCB-28	3.81	3.93	3.93	3.15	3.15	0.92	0.90	0.91
HC	3.25	3.19	3.19	1.85	1.85	0.97	0.97	0.97
Aldrin	3.28	3.29	3.24	0.30	1.22	1.00	1.00	1.00
PCB-52	3.58	3.60	3.74	0.56	4.47	1.00	1.00	1.00
OCS	3.44	3.43	3.38	0.29	1.74	1.00	1.00	1.00
β -HCH	3.05	3.04	3.04	0.33	0.33	1.00	1.00	1.00
HE	3.34	3.35	3.26	0.30	2.40	1.00	1.00	1.00
PCB-101	3.60	3.64	3.74	1.11	3.89	1.00	1.00	1.00
4,4'-DDE	3.35	3.34	3.39	0.30	1.19	0.91	0.90	0.91
Dieldrin	3.23	3.33	3.30	3.10	2.17	0.92	0.91	0.92
PCB-153	3.74	3.68	3.75	1.60	0.27	1.00	1.00	1.00
PCB-138	3.84	3.87	3.89	0.78	1.30	1.00	1.00	1.00
4,4'-DDT	3.21	3.40	3.38	5.92	5.30	1.00	1.00	1.00
PCB-180	3.55	3.68	3.57	3.66	0.56	1.00	1.00	1.00
DCB	3.83	3.81	3.68	0.52	3.92	1.00	1.00	1.00
<i>Column B (DB-5)</i>								
PCBz	2.41	2.43	2.41	0.83	0.00	1.00	1.00	1.00
PCT	2.53	2.54	2.51	0.40	0.79	1.00	1.00	1.00
α -HCH	2.20	2.16	2.24	1.82	1.82	1.00	1.00	1.00
HCB	2.75	2.69	2.71	2.18	1.45	1.00	1.00	1.00
β -HCH	2.80	2.80	2.76	0.00	1.43	1.00	1.00	1.00
γ -HCH	2.27	2.32	2.31	2.20	1.76	1.00	1.00	1.00
PCB-28	3.13	3.27	3.18	4.47	1.60	0.94	0.95	0.94
HC	2.44	2.41	2.38	1.23	2.46	1.00	1.00	1.00
PCB-52	2.70	2.69	2.70	0.37	0.00	1.00	1.00	1.00
Aldrin	2.43	2.45	2.48	0.82	2.06	1.00	1.00	1.00
OCS	2.53	2.57	2.57	1.58	1.58	1.00	1.00	1.00
HE	2.48	2.46	2.52	0.81	1.61	1.00	1.00	1.00
PCB-101	2.81	2.76	2.78	1.78	1.07	1.00	1.00	1.00
Dieldrin	2.54	2.49	2.48	1.97	2.36	0.99	0.99	0.99
4,4'-DDE	2.53	2.52	2.58	0.40	1.98	0.99	0.99	0.99
4,4'-DDD	2.58	2.54	2.54	1.55	1.55	1.00	1.00	1.00
PCB-153	2.88	2.80	2.81	2.78	2.43	1.00	1.00	1.00
4,4'-DDT	2.48	2.51	2.53	1.21	2.02	1.00	1.00	1.00
PCB-138	2.82	2.82	2.83	0.00	0.35	1.00	1.00	1.00
PCB-180	2.78	2.80	2.77	0.72	0.36	1.00	1.00	1.00
DCB	2.63	2.68	2.67	1.90	1.52	1.00	1.00	1.00

$$Err_{1/2} = \frac{|W_{1/2}(x) - W_{1/2}(\text{std})|}{W_{1/2}(\text{std})} \times 100$$

where x represents std1 or std2, $W_{1/2}$ represents half peak width, and std, std1 and std2 mean standard samples.

column A is closer to the bottom limit of 0.95. Therefore, DCB is configured as effective internal standard. The evaluation coefficients of DCB and PCT are assigned to 1 and 0, respectively, which can be seen in Table 5.

The second step is to evaluate the separation status of each component on columns A and B. The ratio K_3 which is the distance from the peak top to valley to the peak height is applied as a parameter to evaluate the separation status for specific chromatographic peak. The relative deviation $Err_{1/2}$ of the half peak width $W_{1/2}$ compared to that in the standard sample was applied to check the repeatability and matrix interference for each component since $W_{1/2}$ always is the same for a definite component under identical chromatographic operating conditions. If it exceeds a certain range, the corresponding calculated concentration should be excluded.

The $W_{1/2}$ and K_3 values of all analytical com-

ponents in three standard samples are shown in Table 4. On columns A and B, the maximum $Err_{1/2}$ values are 5.92 and 4.47%, and the lowest K_3 values are 0.90 and 0.94, respectively. Therefore, we choose 10% and 0.90 as the threshold values for $Err_{1/2}$ and K_3 . If $Err_{1/2}$ is less than 10% and K_3 is larger than 0.90, the evaluation coefficient is assigned to 1. If any one of them is not met, the evaluation coefficient is assigned to 0. The practical application of this rule is shown in detail in Table 5.

Based on the evaluation coefficients from the above two steps, the suitable concentrations are calculated through averaging the effective concentrations for each component. An example of a quantitative report obtained through the above method is shown in Table 5. In columns 2–9 in Table 5, the separation ratios, the half peak widths, the relative deviation of the half peak width and the corresponding evaluation coefficients of each com-

Table 5
Example of a quantitative report obtained by the two-step evaluation method

Compound	K_3^A	$W_{1/2}^A$	$Err_{1/2}^A$	k^A	K_3^B	$W_{1/2}^B$	$Err_{1/2}^B$	k^B	C_{PCT}^A	k_{PCT}^A	C_{DCB}^A	k_{DCB}^A	C_{PCT}^B	k_{PCT}^B	C_{DCB}^B	k_{DCB}^B	C^*
PCBz	1.00	2.50	3.47	1	0.94	3.01	24.90	0	9.53	0	10.68	1	13.86	0	16.50	1	10.68
PCT	1.00	2.88	3.03	1	1.00	2.40	5.14	1	10.00	0	10.00	1	10.00	0	10.00	1	10.00
HCB	1.00	3.01	6.81	1	1.00	2.51	8.73	1	10.90	0	12.19	1	10.26	0	12.17	1	12.18
α -HCH	1.00	2.80	1.41	1	1.00	2.14	2.73	1	9.61	0	10.77	1	9.54	0	11.28	1	11.03
γ -HCH	1.00	2.88	2.70	1	1.00	2.27	0.00	1	9.42	0	10.55	1	9.18	0	10.88	1	10.71
PCB-28	0.96	3.49	8.40	1	1.00	2.79	10.86	0	11.38	0	12.74	1	10.82	0	12.87	1	12.74
HC	0.98	3.30	1.54	1	1.00	2.43	0.41	1	9.21	0	10.31	1	8.94	0	10.63	1	10.47
Aldrin	1.00	3.30	0.61	1	1.00	2.42	0.41	1	9.15	0	10.25	1	8.67	0	10.33	1	10.29
PCB-52	1.00	3.46	3.35	1	1.00	2.62	2.96	1	9.80	0	10.97	1	9.12	0	10.83	1	10.90
OCS	1.00	3.41	0.87	1	1.00	2.49	1.58	1	9.46	0	10.60	1	9.19	0	10.93	1	10.77
β -HCH	1.00	3.01	1.31	1	1.00	2.61	6.79	1	8.63	0	9.67	1	10.44	0	12.42	1	11.04
HE	1.00	3.31	0.90	1	0.97	2.47	0.40	1	9.47	0	10.61	1	8.85	0	10.50	1	10.55
PCB-101	1.00	3.58	0.56	1	1.00	2.68	4.63	1	9.67	0	10.82	1	9.24	0	10.94	1	10.88
4,4'-DDE	0.94	3.28	2.09	1	0.99	2.44	3.56	1	9.42	0	10.55	1	9.10	0	10.80	1	10.68
Dieldrin	0.94	3.34	3.41	1	0.99	2.49	1.97	1	8.98	0	10.05	1	8.57	0	10.16	1	10.11
PCB-153	1.00	3.65	2.41	1	1.00	2.91	1.04	1	8.02	0	8.98	1	9.41	0	11.18	1	10.08
PCB-138	1.00	3.84	0.00	1	0.96	2.80	0.71	1	9.21	0	10.32	1	9.14	0	10.87	1	10.60
4,4'-DDT	0.97	3.65	13.71	0	0.96	2.51	1.21	1	9.21	0	10.31	1	8.69	0	10.34	1	10.34
PCB-180	1.00	3.54	0.28	1	1.00	2.73	1.80	1	9.00	0	10.08	1	8.73	0	10.37	1	10.23
DCB	1.00	3.64	4.96	1	0.99	2.67	1.52	1	17.85	0	20.00	1	16.80	0	20.00	1	20.00
4,4'-DDD					1.00	2.50	3.10	1					8.97	0	10.66	1	10.66

Concentration unit: ng/g. C_{PCT} and C_{DCB} are the calculated concentrations based on PCT and DCB as internal standards, respectively, and k_{PCT} and k_{DCB} are the evaluation coefficients for internal standards PCT and DCB, respectively. Superscript A and B denote column A and B, respectively. C^* is the calculated concentration having considered the evaluation coefficients for two columns and two internal standard, which is calculated as follows:

$$C^* = \frac{k^A(C_{PCT}^A k_{PCT}^A + C_{DCB}^A k_{DCB}^A) + k^B(C_{PCT}^B k_{PCT}^B + C_{DCB}^B k_{DCB}^B)}{k^A(k_{PCT}^A + k_{DCB}^A) + k^B(k_{PCT}^B + k_{DCB}^B)}$$

ponent on columns A and B are listed, respectively. In columns 10–17, the four calculated concentrations based on two internal standards on columns A and B and the corresponding evaluation coefficients of each component for two internal standards on the two columns are listed. Considering the evaluation coefficients of each component on two different columns and those for two internal standards on two columns, a suitable concentration C^* is obtained that is more reasonable than any original value or their average.

5. Conclusions

A data manipulation method has been developed for automatic peak recognition and result evaluation in the analysis of organic chlorinated hydrocarbons with dual-column gas chromatography. It is very convenient and useful in the identification and quantification of individual peaks in the chromatograms of environmental and other relevant samples. The highly accurate peak recognition has been achieved by using the calibrated retention times to recognize the peaks. At the same time, with the two-step evaluation method the evaluation coefficients of each component in a practical sample and suitable quantitative results have been obtained.

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Institute of Chemical Physics, Chinese Academy of Sciences.

References

- [1] K. Oxyinos, J. Schmitzer, A. Kettrup, Guidelines For Environmental Specimen Banking in the Federal Republic of Germany, Federal Environmental Agency, Berlin, 1989.
- [2] Y. Xu, W. Wu, Y. Zang, H. Staudacher, A. Kettrup, C.E.W. Steinberg, *Fresenius Environ. Bull.* 3 (1994) 557.
- [3] M.S. Tabucanon, S. Watanabe, C. Siri Wong, R. Boonyatumanond, H. Twata, R. Tatsukawa, S. Ohgaki, *Water Sci. Technol.* 25 (1992) 17.
- [4] Y. Xu, Y. Zhang, H. Staudacher, A. Kettrup, in: Annual Report of FEBL GSF-Forschungszentrum, Neuherberg, Germany, 1992, p. 87.
- [5] P. Marth, K.-W. Schramm, D. Martens, K. Oxyinos, J. Schmitzer, A. Kettrup, *Int. J. Environ. Anal. Chem.* 75 (1999) 229.
- [6] J. Gandrass, M. Zoll, *Acta Hydrochim. Hydrobiol.* 24 (1996) 212.
- [7] T.P. O'Connor, *Mar. Environ. Res.* 53 (2002) 117.
- [8] R.J. Norstrom, *Organohalogen Comp.* 20 (1994) 541.
- [9] R.J. Norstrom, D.C.G. Muir, *Sci. Total Environ.* 154 (1994) 107.
- [10] F. Kastanek, K. Demnerova, J. Pazlarova, J. Burkhard, Y. Maletterova, *Int. Biodeterioration Biodegradation* 44 (1999) 39.
- [11] V. Lopez-Avila, N. Dodhiwala, W.F. Beckert, J. High Resolut. Chromatogr. Chromatogr. Commun. 11 (1988) 234.
- [12] V. Lopez-Avila, N.S. Dodhiwala, J. Milanes, W.F. Beckert, J. Assoc. Off. Anal. Chem. 72 (1989) 593.
- [13] A. Zybin, K. Niemax, *Anal. Chem.* 69 (1997) 755.
- [14] R.C. Hale, J. Greaves, *J. Chromatogr.* 580 (1992) 257.
- [15] B.G. Oliver, K.D. Nicol, *Chromatographia* 16 (1982) 336.
- [16] K. Oxyinos, H. Schmitzer, H.W. Dürbeck, A. Kettrup, in: M. Rossbach, J.D. Schlodt, P. Ostapczuk (Eds.), *Specimen Banking—Environmental Monitoring and Modern Analytical Approaches*, Springer, Berlin, 1992, p. 127, Chapter 5.3.
- [17] X.M. Liang, W.Z. Wu, K.-W. Schramm, B. Henkelmann, A. Yediler, A. Kettrup, Y.K. Zhang, P.C. Lu, *Fresenius J. Anal. Chem.* 354 (1996) 362.
- [18] W. Wang, X. Liang, W. Wu, K.-W. Schramm, B. Henkelmann, Y. Xu, A. Kettrup, *Chemosphere* 40 (2000) 601.