Journal of Chromatography B, 898 (2012) 38–52

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

Simultaneous determination of pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and phthalate esters in human adipose tissue by gas chromatography–tandem mass spectrometry

Na Wang[a,b], Deyang Kong[a,b], Zhengjun Shan[a,b], Lili Shi[a,b,*], Daoji Cai[a,b], Yanzhong Cao[c], Yongming Liu[c], Guofang Pang[c]

[a] Nanjing Institute of Environmental Science, Ministry of Environmental Protection of China, Nanjing 210042, China
[b] Key Laboratory of Pesticide Environmental Assessment and Pollution Control, Ministry of Environmental Protection of China, Nanjing 210042, China
[c] Technological Center of Qin huangdao Entry-Exit Inspection and Quarantine Bureau, Qinhuangdao 066002, China

ARTICLE INFO

Article history:
Received 7 February 2012
Accepted 7 April 2012
Available online 15 April 2012

Keywords:
Pesticides
Polycyclic aromatic hydrocarbons (PAHs)
Polychlorinated biphenyls (PCBs)
Phthalate esters (PAEs)
GC–MS/MS

ABSTRACT

This paper describes a method for the simultaneous determination of 284 environmental contaminants, including 57 pesticides, 15 polycyclic aromatic hydrocarbons (PAHs), 209 polychlorinated biphenyls (PCBs) and 3 phthalate esters (PAEs), in adipose tissue samples. For the first time, a gas chromatography–tandem mass spectrometry (GC–MS/MS) method following a homogenised extraction using acetonitrile and purification by gel permeation chromatography (GPC) was used. Various performance characteristics, such as the limit of detection (LOD), limit of quantification (LOQ), linear range, recovery and precision, were determined for each analyte. The LOD for most analytes was below 0.01 mg/kg. The recoveries and relative standard deviations (RSDs) were determined by spiking untreated samples with the analytes at the LOQ, 2 × LOQ and 4 × LOQ levels. The average recovery for most pesticides was between 70% and 120% and the precision values, expressed as RSD, were all below 20.4% ($n = 6$). This method may provide an efficient tool for evaluating the extent of exposure to organic contaminants using human adipose tissue.

1. Introduction

While we enjoy the numerous benefits afforded to us by a large number of organic compounds, including pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and phthalate esters (PAEs), we often suffer from negative health effect caused by our exposure to them through their introduction into the environment and their ubiquitous presence in our daily lives. Pesticides are substances that play a crucial role in pest management; however, it is important to remember that all pesticides should also be considered active poisons [1]. PAHs and PCBs are persistent organic pollutants with well-known carcinogenic, mutagenic and teratogenic effects in humans and wildlife [2]. PAEs are used as plasticisers for improving the flexibility and workability of polymeric materials, which are produced in large quantities globally [3]. Certain PAEs (e.g., DEHP and D*n*BP) and their metabolites are suspected to be carcinogenic and endocrine disrupting [4–6]. Most of these organic compounds have a tendency to bioaccumulate and have low rates of biodegradation; consequently, they could represent an environmental and human health risk [7].

Recently, the utilisation of human samples for evaluating the extent of exposure to these organic contaminants has become a major focus of research in biological monitoring. Most recent reports have focussed on breast milk and serum samples because these samples are conveniently and inexpensively obtained. However, for an accurate assessment of exposure, monitoring the levels of contaminants in adipose tissue is essential. Therefore, it is necessary to establish an analytical method for the simultaneous determination of a large number of contaminants in adipose tissue.

In recent reports on analytical methods, the analytical targets for biosamples have been limited to several selected organochlorine pesticides and PCBs; none of these studies have satisfied the requirement for the simultaneous analysis of a large number of different adipose tissue contaminants [8–10]. In the field of food analysis, there have been a number of reports on the simultaneous determination of pesticides in various food types, including matrices of vegetable origin, such as tea, leeks and grapes [11–13], as well as matrices containing high amounts of fat, such as animal-based food and fish feed [14,15]. However, these food analyses primarily focussed on pesticides, which are detected by liquid

* Corresponding author at: 8 Jiang-wang-miao Street, Nanjing 210042, China. Tel.: +86 25 8528 7074; fax: +86 25 8528 7074.
E-mail addresses: wangna@nies.org (N. Wang), sll@nies.org (L. Shi).

1570-0232/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jchromb.2012.04.012

Table 1
MRM transitions of 284 analytes in the GC–MS/MS method.

Number	Name	t_R (min)	Quantification ion	Qualification ion	Collision energy (V)
	Heptachlor (ISTD)	22.04	353/263	353/263;353/282	17;17
Group A					
1	PCB 001	11.04	188/152	188/152;188/153	20;10
2	PCB 004	13.39	152/151	152/151;152/150	20;40
3	PCB 008	14.91	224/152	224/152;224/151	30;50
4	PCB 019	15.77	256/221	256/221;256/186	10;20
5	PCB 012	16.55	222/152	222/152;222/151	30;50
6	PCB 027	16.94	186/151	186/151;186/150	20;30
7	PCB 016	17.4	256/186	256/186;256/221	20;10
8	PCB 025	17.93	256/186	256/186;256/151	30;40
9	PCB 021	18.6	256/186	256/186;186/151	20;20
10	PCB 020	18.81	186/151	186/151;186/150	20;30
11	PCB 036	19.24	186/151	186/151;186/150	20;30
12	PCB 043	19.57	294/222	294/222;294/150	30;50
13	PCB 065	19.67	292/222	292/222;292/220	20;20
14	PCB 104	19.84	254/184	254/184;254/219	30;20
15	PCB 072	20.52	292/220	292/220;292/150	30;50
16	PCB 103	20.73	326/256	326/256;326/184	40;50
17	PCB 041	20.93	292/220	292/220;292/150	30;50
18	PCB 067	21.22	292/220	292/220;292/185	30;40
19	PCB 040	21.43	292/220	292/220;292/150	30;50
20	PCB 074	21.57	290/220	290/220;290/150	20;50
21	PCB 102	21.72	254/184	254/184;254/219	30;20
22	PCB 095	21.97	254/184	254/184;254/219	30;20
23	PCB 092	22.46	184/149	184/149;328/256	20;40
24	PCB 099	22.77	326/184	326/184;326/256	50;50
25	PCB 084	22.92	254/184	254/184;254/219	30;20
26	PCB 109	23.24	326/184	326/184;326/256	50;40
27	PCB 083	23.42	184/149	184/149;184/123	20;30
28	PCB 086	23.53	326/291	326/291;326/256	10;20
29	PCB 125	23.66	254/184	254/184;254/219	20;20
30	PCB 087	23.87	328/256	328/256;328/258	30;30
31	PCB 110	24.29	324/254	324/254;324/184	30;50
32	PCB 135	24.58	325/290	325/290;325/288	10;10
33	PCB 124	24.83	326/256	326/256;326/254	30;30
34	PCB 123	24.97	328/256	328/256;328/258	35;35
35	PCB 118*	25.13	326/256	326/256;326/254	30;30
36	PCB 134	25.31	325/290	325/290;325/288	10;10
37	PCB 114	25.45	254/184	254/184;254/219	20;20
38	PCB 168	25.69	358/218	358/218;358/288	50;40
39	PCB 127	26.27	326/256	326/256;326/254	20;20
40	PCB 137	26.43	362/290	362/290;362/292	25;25
41	PCB 163	26.86	360/290	360/290;360/288	30;30
42	PCB 178	26.93	396/326	396/326;396/324	30;30
43	PCB 187	27.25	396/361	396/361;396/359	10;10
44	PCB 162	27.7	358/288	358/288;358/218	30;50
45	PCB 202	28.07	432/360	432/360;432/362	30;30
46	PCB 204	28.3	432/360	432/360;432/362	30;30
47	PCB 197	28.58	428/358	428/358;428/356	30;30
48	PCB 192	28.96	396/324	396/324;396/326	40;40
49	PCB 193	29.31	324/254	324/254;324/252	30;30
50	PCB 190	30.19	394/324	394/324;394/322	20;20
51	PCB 169	30.48	358/288	358/288;362/290	20;20
52	PCB 195	31.18	428/358	428/358;428/356	30;30
53	PCB 206	32.44	466/394	466/394;466/396	40;40
54	PCB 209*	32.78	500/429	500/429;500/428	30;30
Group B					
55	PCB 002	12.46	188/152	188/152;188/151	30;50
56	PCB 007	14.07	224/152	224/152;152/151	10;20
57	PCB 005	14.97	222/152	222/152;152/151	10;20
58	PCB 011	16.34	224/152	224/152;224/151	20;50
59	PCB 013	16.63	152/151	152/151;152/150	20;40
60	PCB 032	17.23	256/186	256/186;256/151	30;40
61	PCB 029	17.42	256/151	256/151;256/150	40;50
62	PCB 050*	17.94	292/220	292/220;292/222	40;40
63	PCB 053	18.68	292/150	292/150;292/220	50;50
64	PCB 022	19.11	256/186	256/186;256/151	20;40
65	PCB 073	19.44	290/220	290/220;290/150	30;50
66	PCB 039	19.61	258/151	258/151;258/186	50;40
67	PCB 062	19.68	292/222	292/222;292/150	20;50
68	PCB 038	19.93	258/151	258/151;258/186	30;50
69	PCB 035	20.55	186/151	186/151;186/150	20;30
70	PCB 064	20.83	220/150	220/150;294/222	30;20
71	PCB 037	20.97	186/151	186/151;186/150	20;30
72	PCB 080	21.39	292/220	292/220;292/150	30;50

Table 1 (*Continued*)

Number	Name	t_R (min)	Quantification ion	Qualification ion	Collision energy (V)
73	PCB 058	21.45	292/222	292/222;292/220	20;20
74	PCB 121	21.57	328/256	328/256;328/258	40;40
75	PCB 093	21.76	326/291	326/291;326/289	10;10
76	PCB 066	22	292/220	292/220;292/222	20;20
77	PCB 090	22.58	324/254	324/254;326/291	30;10
78	PCB 113	22.82	324/254	324/254;326/256	30;20
79	PCB 089	22.93	254/184	254/184;254/219	30;20
80	PCB 152	23.26	358/288	358/288;358/218	30;50
81	PCB 145	23.45	290/218	290/218;290/220	30;30
82	PCB 115	23.59	326/256	326/256;326/254	35;35
83	PCB 154	23.66	358/288	358/288;358/218	40;50
84	PCB 085	23.97	326/256	326/256;326/254	40;40
85	PCB 151	24.36	358/288	358/288;358/323	30;10
86	PCB 139	24.67	358/288	358/288;358/218	30;50
87	PCB 140	24.86	360/325	360/325;360/290	10;20
88	PCB 107	25.04	254/184	254/184;254/219	30;20
89	PCB 143	25.2	290/218	290/218;290/220	30;30
90	PCB 142	25.32	362/237	362/290;362/237	10;20
91	PCB 146	25.45	358/288	358/288;358/323	20;10
92	PCB 122	25.76	326/256	326/256;326/254	40;41
93	PCB 141	26.28	290/218	290/218;290/220	30;30
94	PCB 130	26.67	358/288	358/288;358/218	50;50
95	PCB 138*	26.87	360/290	360/290;360/288	30;30
96	PCB 175	26.97	359/324	359/324;359/322	10;10
97	PCB 183	27.42	396/361	396/361;396/359	10;10
98	PCB 166	27.8	362/290	362/290;362/292	20;20
99	PCB 128	28.09	325/290	325/290;325/288	10;10
100	PCB 200*	28.34	428/358	428/358;428/356	30;30
101	PCB 173	28.74	396/361	396/361;396/359	10;10
102	PCB 157	29.05	360/290	360/290;362/290	30;30
103	PCB 191	29.4	396/326	396/326;396/324	30;30
104	PCB 203	30.26	358/288	358/288;358/286	40;40
105	PCB 208*	30.73	462/392	462/392;462/390	30;30
106	PCB 194	31.77	358/288	358/288;358/286	30;30
Group C					
107	PCB 003*	12.66	188/152	188/152;188/153	20;10
108	PCB 009	14.09	224/152	224/152;224/151	20;40
109	PCB 014	15.27	222/152	222/152;222/151	20;50
110	PCB 018	16.47	186/151	186/151;186/150	20;30
111	PCB 024	16.82	258/151	258/151;258/150	50;50
112	PCB 023	17.29	186/151	186/151;186/150	20;30
113	PCB 054	17.87	292/222	292/222;292/220	30;30
114	PCB 031	18.19	258/151	258/151;258/166	50;50
115	PCB 033*	18.73	258/186	258/186;258/188	20;20
116	PCB 069	19.18	294/222	294/222;220/150	20;40
117	PCB 075	19.52	292/220	292/220;292/150	30;50
118	PCB 046	19.62	292/220	292/220;292/222	30;30
119	PCB 047	19.7	290/220	290/220;290/255	20;20
120	PCB 044	20.48	292/150	292/150;292/220	50;40
121	PCB 042	20.56	294/222	294/222;294/150	30;50
122	PCB 071	20.84	294/220	294/220;220/150	20;40
123	PCB 096	21.02	324/254	324/254;328/256	20;20
124	PCB 088	21.39	328/256	328/256;328/258	40;40
125	PCB 094	21.46	254/184	254/184;254/219	30;20
126	PCB 098	21.67	254/184	254/184;254/219	20;20
127	PCB 076	21.85	220/150	220/150;294/222	30;20
128	PCB 091	22.13	328/256	328/256;328/258	30;30
129	PCB 101*	22.66	328/256	328/256;328/293	30;10
130	PCB 056	22.84	290/220	290/220;290/150	30;50
131	PCB 119	23.01	326/256	326/256;326/254	40;40
132	PCB 079	23.31	220/150	220/150;294/222	30;20
133	PCB 116	23.48	328/256	328/256;328/258	30;30
134	PCB 117	23.59	328/256	328/256;328/258	40;40
135	PCB 078	23.72	294/222	294/222;294/150	30;50
136	PCB 136	23.99	362/290	362/290;362/292	20;20
137	PCB 144	24.48	360/290	360/290;360/288	30;30
138	PCB 077	24.77	290/220	290/220;290/150	30;50
139	PCB 149	24.86	360/325	360/325;360/290	10;20
140	PCB 188	25.06	324/254	324/254;324/252	30;30
141	PCB 133	25.22	358/288	358/288;358/323	30;20
142	PCB 165*	25.39	358/218	358/218;358/288	50;40
143	PCB 161	25.47	362/290	362/290;362/292	20;20
144	PCB 132	26.08	360/290	360/290;360/288	25;25
145	PCB 105	26.34	254/184	254/184;254/219	30;20
146	PCB 186	26.69	324/254	324/254;324/252	30;30
147	PCB 158	26.92	290/218	290/218;290/220	30;30

Table 1 (*Continued*)

Number	Name	t_R (min)	Quantification ion	Qualification ion	Collision energy (V)
148	PCB 182	27.16	398/326	398/326;398/328	30;30
149	PCB 159	27.44	358/288	358/288;362/290	20;20
150	PCB 167	27.91	358/218	358/218;358/288	50;40
151	PCB 174	28.17	324/254	324/254;324/252	30;30
152	PCB 177	28.44	394/324	394/324;394/322	30;30
153	PCB 156	28.82	362/290	362/290;360/290	30;40
154	PCB 180*	29.23	396/324	396/324;396/326	30;30
155	PCB 198	30.01	430/360	430/360;430/358	30;30
156	PCB 196	30.27	358/288	358/288;358/286	30;30
157	PCB 207	30.94	464/463	464/463;464/394	10;30
158	PCB 205	31.9	430/360	430/360;430/358	20;20
Group D					
159	PCB 010*	13.27	152/151	152/151;152/150	20;40
160	PCB 006	14.67	152/151	152/151;152/150	20;40
161	PCB 030	15.5	186/151	186/151;186/150	20;30
162	PCB 017	16.48	221/186	221/186;221/151	20;40
163	PCB 015	16.91	222/152	222/152;222/151	20;40
164	PCB 034	17.39	258/186	258/186;258/188	20;20
165	PCB 026	17.89	258/186	258/186;258/151	20;40
166	PCB 028*	18.22	256/151	256/151;256/150	50;50
167	PCB 051	18.8	294/222	294/222;294/224	30;30
168	PCB 045	19.2	220/150	220/150;220/185	30;20
169	PCB 052*	19.56	220/150	220/150;220/185	30;20
170	PCB 049	19.64	290/220	290/220;290/185	40;40
171	PCB 048	19.75	220/150	220/150;220/185	10;10
172	PCB 059	20.49	220/150	220/150;220/185	30;20
173	PCB 068	20.62	294/222	294/222;294/220	30;30
174	PCB 100	20.87	328/256	328/256;328/184	30;50
175	PCB 057	21.05	220/150	220/150;220/185	30;20
176	PCB 063	21.41	292/220	292/220;292/222	30;30
177	PCB 061	21.47	294/222	294/222;294/150	30;50
178	PCB 155	21.7	360/290	360/290;360/288	30;30
179	PCB 070	21.91	294/222	294/222;220/150	20;40
180	PCB 055	22.42	292/222	292/222;292/220	20;20
181	PCB 060	22.76	294/222	294/222;294/224	20;20
182	PCB 150	22.85	325/290	325/290;325/288	10;10
183	PCB 112	23.15	326/256	326/256;326/254	30;30
184	PCB 148	23.39	362/327	362/327;362/290	10;20
185	PCB 111	23.49	324/254	324/254;328/256	20;20
186	PCB 097	23.65	328/256	328/256;328/293	20;20
187	PCB 120	23.73	254/184	254/184;254/219	20;20
188	PCB 081*	24.21	290/220	290/220;290/150	30;50
189	PCB 147	24.57	290/218	290/218;290/220	30;30
190	PCB 082	24.82	328/256	328/256;328/258	40;40
191	PCB 108	24.95	254/184	254/184;254/219	30;20
192	PCB 106	25.1	328/256	328/256;328/184	40;50
193	PCB 184	25.31	396/326	396/326;396/324	30;30
194	PCB 131	25.44	360/290	360/290;360/288	30;30
195	PCB 153*	25.67	290/218	290/218;290/220	20;20
196	PCB 179	26.14	398/326	398/326;398/328	20;20
197	PCB 176	26.39	324/254	324/254;324/252	40;40
198	PCB 160	26.85	360/290	360/290;360/288	20;20
199	PCB 164	26.92	360/290	360/290;360/288	20;20
200	PCB 129	27.23	325/290	325/290;325/218	10;40
201	PCB 126	27.69	254/184	254/184;254/220	30;20
202	PCB 185	27.92	394/320	394/322;394/320	30;30
203	PCB 181	28.17	394/324	394/324;394/322	30;30
204	PCB 171	28.49	398/326	398/326;398/328	30;30
205	PCB 172	28.93	394/324	394/324;394/322	30;30
206	PCB 199	29.27	358/288	358/288;358/286	40;40
207	PCB 201	30.13	432/360	432/360;432/361	30;30
208	PCB 170	30.36	359/324	359/324;359/322	20;20
209	PCB 189	31.02	394/324	394/324;394/322	20;20
Group E					
210	Naphthalene*	6.41	128/101	128/101;128/77	15;15
211	Isoprotuton*	6.58	146/128	146/128;146/91	15;15
212	Dichlorvos*	7.88	185/93	185/93;185/109	15;10
213	Carbofuran*	8.36	164/149	164/149;164/103	15;25
214	Methamidophos*	9.35	141/95	141/95;141/80	10;15
215	Acenaphthylene*	10.55	152/126	152/126;151/99	15;25
216	Acenaphthene*	10.85	152/126	152/126;151/99	15;25
217	Fluorene	12.94	165/164	165/164;165/163	25;25
218	Hexachlorobenzene*	14.36	284/249	284/249;284/214	18;25
219	Ethoprophos	14.4	158/97	158/97;158/114	12;7
220	Chlordimeform*	14.91	196/181	196/181;196/152	5;25
221	Trifluralin*	15.37	306/264	306/264;306/206	12;15

Table 1 (*Continued*)

Number	Name	t_R (min)	Quantification ion	Qualification ion	Collision energy (V)
222	α-HCH*	16.14	219/183	219/183;219/147	5;15
223	Omethoate*	16.82	156/110	156/110;156/80	5;10
224	Anthracene*	17.03	176/150	176/150;178/152	20;12
225	Clomazone*	17.04	204/107	204/107;204/78	25;25
226	Diazinon*	17.09	304/179	304/179;304/162	8;8
227	Phenathrene	17.13	178/150	178/150;178/151	45;40
228	γ-HCH*	17.72	219/183	219/183;219/147	5;15
229	Atrazine*	17.95	215/173	215/173;215/200	5;5
230	Simazine*	18.03	201/173	201/173;201/138	5;15
231	Heptachlor*	18.4	272/237	272/237;272/235	25;25
232	Pirimicarb*	18.98	238/166	238/166;238/96	15;25
233	Dimethoate*	19.32	125/79	125/79;143/111	8;12
234	Aldrin	19.41	263/193	263/193;263/191	25;35
235	Alachlor*	20.16	237/160	237/160;237/146	8;20
236	Prometryne*	20.19	241/199	241/199;241/184	5;5
237	Chlorothalonil*	20.35	266/231	266/231;266/170	20;35
238	Phthalic acid bis-butyl ester	20.69	149/121	149/121;149/93	10;10
239	β-HCH*	20.72	219/183	219/183;219/147	10;20
240	Chlorpyrifos*	20.92	314/286	314/286;314/258	5;5
241	Parathion-methyl*	21.05	263/109	263/109;263/246	12;5
242	Dicofol*	21.34	250/139	250/139;250/215	15;10
243	Metolachlor*	21.44	238/162	238/162;238/133	15;25
244	δ-HCH*	21.5	219/183	219/183;219/147	10;20
245	Triadimefon*	22.42	210/183	210/183;210/129	5;10
246	Fluoranthene*	22.58	202/152	202/152;202/176	30;30
247	2,4′-DDE	22.7	246/176	246/176;246/211	25;25
248	Cis-chlordane*	23.21	373/266	373/266;373/301	12;12
249	Phenthoate*	23.38	274/246	274/246;274/121	5;25
250	Trans-chlordane*	23.5	373/266	373/266;373/301	12;12
251	Pyrene	23.62	202/199	202/199;202/200	45;40
252	4,4′-DDE	23.9	246/176	246/176;246/211	25;25
253	Butachlor	23.98	176/150	176/150;176/126	25;25
254	Dieldrin	24.47	277/241	277/241;277/207	12;12
255	2,4′-DDD	25.04	235/165	235/165;235/199	15;15
256	Buprofezin	25.05	105/77	105/77;172/116	18;7
257	Endrin*	25.06	263/191	263/191;263/193	20;12
258	2,4′-DDT*	25.47	235/165	235/165;235/199	25;25
259	Nithophen*	26.27	283/162	283/162;283/202	25;25
260	Oxyfluorfen*	26.45	300/223	300/223;188/144	18;17
261	4,4′-DDD	26.73	235/165	235/165;235/199	15;15
262	4,4′-DDT*	27.23	235/199	235/199;235/165	25;25
263	Phthalic acid benzyl butyl ester*	27.84	206/149	206/149;149/65	5;25
264	Propargite*	28.08	173/117	173/117;173/145	10;10
265	Tricyclazole*	28.39	189/162	189/162;189/135	10;15
266	Triazophos*	28.54	161/134	161/134;161/106	8;15
267	Mirex*	28.7	272/237	272/237;272/235	15;15
268	Benzo(a)anthrancene*	29.27	228/226	228/226;228/202	30;30
269	Phthalic acid bis-2-ethylhexyl ester	29.47	167/149	167/149;167/65	10;25
270	Amitraz*	30.37	293/162	293/162;293/132	5;15
271	Lamba-cyhalothrin*	31.41	197/141	197/141;197/161	15;5
272	Pyridaben*	32.07	147/117	147/117;147/132	25;15
273	Benzo(b)fluoranthene*	32.94	252/250	252/250;252/224	40;50
274	Benzo(k)fluoranthene*	32.94	252/250	252/250;252/224	40;50
275	Cyfluthrin*	33.33	206/151	206/151;206/177	15;20
276	Cypermethrin*	33.53	163/127	163/127;163/91	5;10
277	Benzo(a)pyrene*	33.7	252/250	252/250;252/226	25
278	Acetamiprid*	33.78	152/116	152/116;166/139	20;8
279	Fenvalerate-1*	34.61	419/225	419/225;419/167	5;5
280	Fenvalerate-2*	34.96	419/225	419/225;419/167	5;5
281	Deltamethrin*	35.98	181/152	181/152;181/127	25;25
282	Indeno(1,2,3-cd)pyrene*	37.63	276/274	276/274;276/248	40;50
283	Dibenzo[a,h]anthracene*	37.83	278/276	278/276;278/274	40;55
284	Benzo(g,h,i)peryene*	38.64	274/272	274/272;274/248	25;25

Note: (*) denotes the 77 representative chemicals which were tested to optimise the extraction and cleanup condition.

chromatography–mass spectrometric (LC–MS) methods, rather than the various other environmental contaminants [16,17]. To the best of our knowledge, there are no previous studies reporting multi-residue methods for determining the burdens of large numbers of contaminants, including pesticides, PAHs, PCBs and PAEs, in adipose samples via gas chromatography–tandem mass spectrometry (GC–MS/MS).

Basically, this analytical method for environmental contaminants is based on both gas chromatography (GC) coupled to either mass spectrometry (MS) or tandem mass spectrometry (MS/MS) and liquid chromatography electrospray ionisation mass spectrometry (LC–ESI-MS) or LC–MS/MS. GC seems to be the technical choice for the analysis of environmental contaminants for chemicals which are thermally stable or volatile, while LC, as a complementary method to GC, offers an alternative and powerful tool for determining the amounts of such compounds [11]. However, the sensitivity of GC–MS/MS is much higher than that of LC–MS/MS for most chemicals suited for detection by GC.

The present paper describes, for the first time, a method for the simultaneous determination of 284 environmental contaminants, including 57 pesticides, 15 PAHs, 209 PCBs and 3 PAEs, in adipose tissue samples using a GC–MS/MS method following a homogenised extraction using acetonitrile and purification by gel permeation chromatography (GPC).

2. Experimental

2.1. Reagents, chemicals and materials

Acetonitrile, acetone, n-hexane, cyclohexane, isooctane, ethyl acetate, dichloromethane, methylbenzene and methanol of pesticide residue, were obtained from Merck (Darmstadt, Germany). Anhydrous sodium sulphate (Shanghai, China) was baked at 650 °C for 4 h and stored in a desiccator until used. Certified chemical standards (Table 1) of the pesticides, PAHs, PCBs and PAEs, with purities ranging from 95% to 99.9%, were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Stock standard solutions were prepared by accurately weighing individual chemical standards (5–10 mg, accurate to 0.1 mg) into 10 mL volumetric flasks and diluting to the appropriate volumes with methylbenzene, n-hexane, acetone, isooctane or methanol, depending on the solubility of the compound. Heptachlor epoxide was prepared in methylbenzene and used as the internal standard solution. Mixed standard solutions were prepared, according to the sensitivity of the instrument for each compound, by placing various amounts of the individual stock standard solutions in a 50 mL volumetric flasks and diluting with methylbenzene. The mixed standard solutions were stored in the dark at 4 °C until used.

A Sep-Pak® NH_2-Carb column (0.5 g/6 mL) and Sep-Pak® Al_2O_3 column (2 g/12 mL) were purchased from Waters Inc. (USA). An ENVITM-18 column (2 g/12 mL) was purchased from Supelco Inc. (USA). Microporous membrane filter (0.45 μm, φ13 mm, organic) was purchased from Truelab Inc. (China).

2.2. Sample preparation

Blank fat tissue samples for the validation of the method were collected from the abdominal region of Chinese pigs with good health status from a local slaughterhouse. The age of the pigs was about 0.5 years old. The same amounts of fat tissue samples from pigs with different gender were mixed and stored at −20 °C. A total of 5 ± 0.01 g of adipose tissue sample was homogenised at 15,000 rpm twice with 35 mL of acetonitrile (plus 15 g of anhydrous sodium sulphate) in a homogeniser. After centrifuging for 5 min at 4200 rpm, the supernatant was collected through a funnel filled with anhydrous sodium sulphate and then concentrated to approximately 2 mL on a rotary-evaporator at 45 °C. Solvent exchange was conducted twice using 7 mL of cyclohexane–ethyl acetate (1–1, v/v) until the volume of the final solution was approximately 1 mL.

After mixing with the internal standard solution, the final concentrated solution was transferred to a glass vial and diluted to 10 mL with cyclohexane–ethyl acetate (1–1, v/v). This solution was filtered through a 0.45 μm membrane and transferred to a glass vial for clean-up.

2.3. Sample clean-up

To remove fat and other potential matrix obstructions, a cleanup was performed using an automated GPC cleanup system (J2 Scientific AccuPrep MPS™). Bio-Beads S-X3 were packed into the glass column (360 mm × 25 mm i.d.). The organic mobile phase of the GPC was cyclohexane–ethyl acetate (1–1, v/v) in the isocratic mode. The flow rate was 4.7 mL/min, the detection wavelength was 254 nm and the injection volume was 5 mL. The fraction from 23 to 60 min was collected and then evaporated to 1 mL in the liquid level sensor mode.

2.4. GC–MS/MS set up

The final samples were analysed by GC–MS/MS using an Agilent 7890 gas chromatograph coupled with a Waters Quattro micro triple quadrupole MS/MS operating in the electron ionisation (EI) mode. The final sample extract (1 μL) was injected in the splitless mode onto a DB-1701 capillary column (30 m × 0.25 mm × 0.25 μm; Agilent, USA) using helium as the carrier gas at a constant flow rate of 1.2 mL/min. The injector temperature was 290 °C, and the interface temperature was 250 °C. The oven temperature programme was set as follows: holding for 1 min at 40 °C before first ramping at 30 °C/min to 130 °C, then 5 °C/min to 250 °C and finally 10 °C/min to 300 °C and holding for 5 min. The ionisation energy was 70 eV. The acquisition mode was a multiple reaction monitor (MRM) with 2 parent-product ion transitions being monitored for quantification and quality. The retention time, quantitative ions and qualitative ions for each compound are given in Table 1.

3. Results and discussion

3.1. Optimisation of the extraction procedure

3.1.1. Selection of the extracting solvents

Seven extracting solvents, n-hexane, n-hexane–acetone (1–1, v/v), n-hexane–acetone (3–1, v/v), cyclohexane–ethyl acetate (1–1, v/v), n-hexane–dichloromethane (4–1, v/v), acetonitrile and acetic acid–acetonitrile (1–100, v/v), were initially selected to extract the 77 representative chemicals (specially marked by "*" in Table 1). The extraction efficiencies of the experimental procedure were determined using pig adipose samples fortified to a level of 2 × LOQ (n = 3). The comparative results (see in Fig. 1) showed better efficiencies for extractions using acetonitrile, cyclohexane–ethyl acetate (1–1, v/v), n-hexane–acetone (3–1, v/v) and n-hexane–dichloromethane (4–1, v/v), which yielded similar efficiencies for most of the chemicals, whereas the extraction efficiency of acetic acid–acetonitrile (1–100, v/v) was poor, indicating that acidic conditions were unsuitable for these extractions. For most of the chemicals, the relative standard deviation of the extraction efficiencies for acetonitrile was lower than those for the other solvents. Moreover, less fat was found in the acetonitrile extract than in the other three solvent systems. Therefore, acetonitrile was chosen as the extraction solvent for further method optimisation and evaluation.

3.1.2. Comparison of the extraction methods

A comparison of various extraction methods, such as accelerated solvent extraction (ASE), shaking extraction and homogenisation using acetonitrile as the extraction solvent, is shown in Fig. 2 and clearly indicates that homogenisation had the best efficiencies. Although ASE is generally thought of as a highly automated and efficient extraction method, the experiments in our study showed that more fatty compounds were extracted under the high pressure and temperature conditions associated with ASE, which resulted in extensive matrix interference. Therefore, the simpler homogenisation method using 5 g samples was selected as the extraction method for the present study.

3.2. Optimisation of the cleanup procedure

3.2.1. Comparison of the cleanup methods

The accurate analysis of adipose tissue samples requires an efficient extraction-cleanup method because the concentrated sample

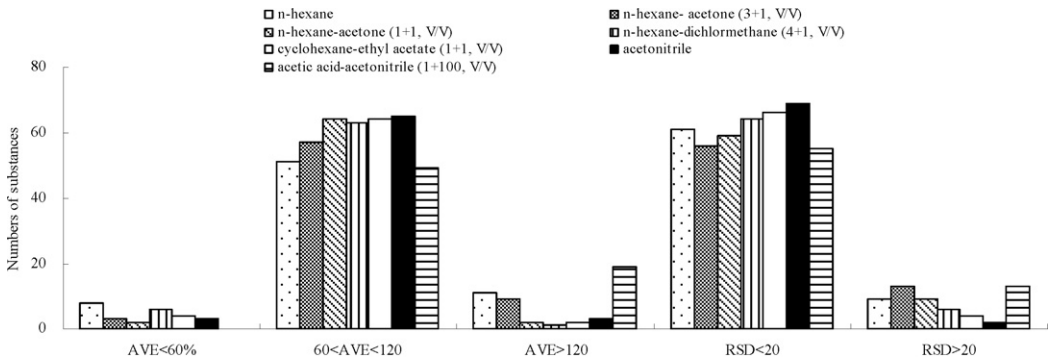

Fig. 1. Comparative efficiencies of extraction by different solvents with 77 representative substances which were specifically marked by "*" in Table 1.

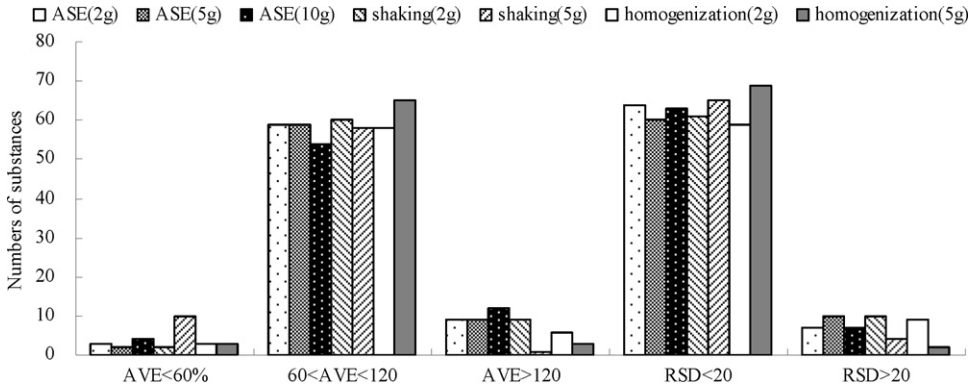

Fig. 2. Comparative efficiencies of different methods with 77 representative substances which were specifically marked by "*" in Table 1.

extracts contain a large quantity of co-extracted lipids that can interfere with detection or damage the capillary column [15]. In addition, the elimination of interfering substances and reduced background noise obtained via an efficient cleanup step allows for both high precision and high accuracy in the determination of analytes. SPE and GPC were tested as cleanup techniques. To study the effectiveness of SPE, three different sorbent systems (Sep-Pak® NH_2-Carb, Sep-Pak® $Al_2O_3 + NH_2$-Carb and ENVITM-18 + NH_2-Carb) were assayed using acetonitrile–methylbenzene (3–1, v/v) as the elution solvent during the cleanup step. An internal standard was added to the extracts at the beginning of the cleanup procedure to monitor the critical stages of the cleanup process. The analytical result showed that while both $Al_2O_3 + NH_2$-Carb and ENVITM-18 + NH_2-Carb combinations yielded clean extracts, the procedure was tedious and the recoveries were low. A comparison of the recoveries and RSDs of the different cleanup methods is shown in Fig. 3. The analysis of samples spiked to the same concentration levels and purified by both an NH_2-Carb column and GPC showed comparatively good recovery values, but the cleanup effectiveness was better for GPC than for the NH_2-Carb column, which was clearly shown by the GC–MS–MS total ion chromatograms of samples cleaned by the different procedures (see Fig. 4). Therefore, GPC was selected as the final cleanup procedure for the present study.

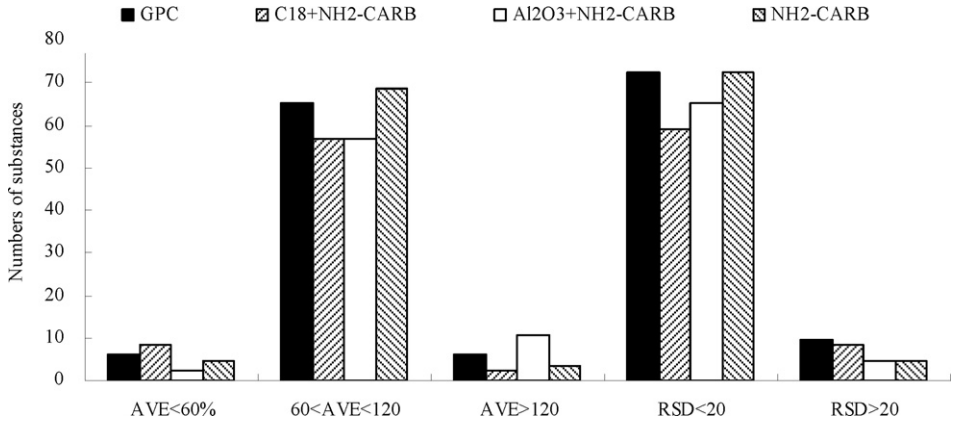

Fig. 3. Comparative efficiencies of different cleanup methods with 77 representative substances which were specifically marked by "*" in Table 1.

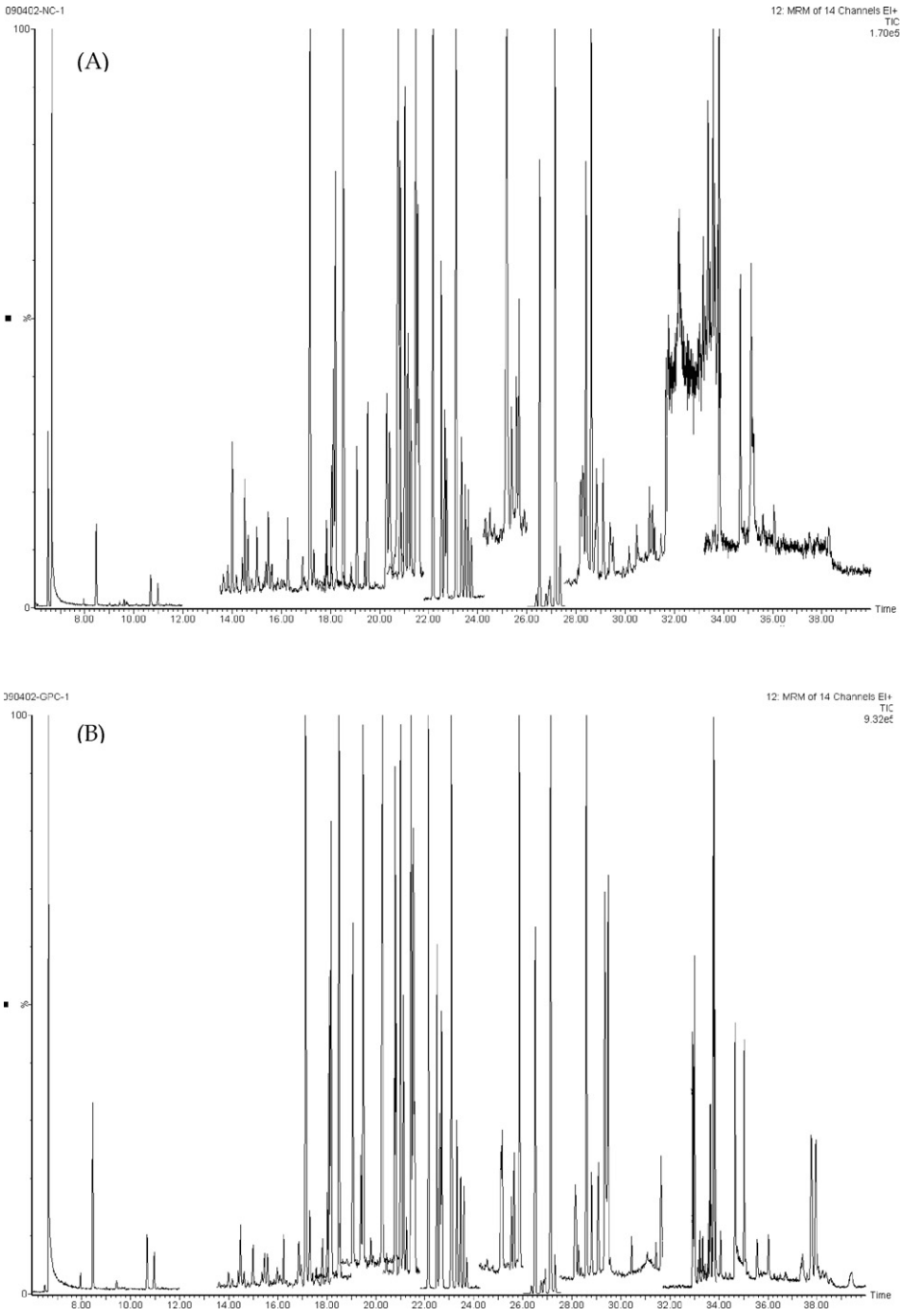

Fig. 4. Total ion chromatograms of spiked pig fat samples purified by NH2-Carb (A) and GPC (B).

3.2.2. GPC conditions

To assure that all chemicals were collected from the GPC cleaning step, eluting chromatograms for each of the chemical standard solutions, the pig adipose sample fortified with the mixed chemicals and the blank pig adipose samples were recorded using a GPC UV detector. These chromatograms showed that the fatty compounds and analytes were effectively separated by GPC elution (Fig. 5).

It can be seen from Fig. 5 that the elution time of the fatty compounds was between 14 and 23 min whereas the elution time for most of the analytes was between 28 and 50 min. Therefore, a representative fraction from 23 to 60 min was collected for the final instrument analysis.

3.3. Optimisation of the GC–MS/MS conditions

Selecting the appropriate GC–MS/MS analysis conditions, which includes choosing the quantitative and qualitative ions for each target compound, is of great importance. In addition, the optimisation of the collision energies was required to identify the chromatographic peaks for each target compound. The precursor ions were selected for each of the 284 analytes based on their retention times, which were analysed in the full scan mode over the m/z range of 50–500 and carefully fragmented by applying various collision energies in the range of −10 to −50 V to generate the MS/MS product ions that provide the desired quantitative structural information (see Table 1). A quantitative ion and two qualitative ions

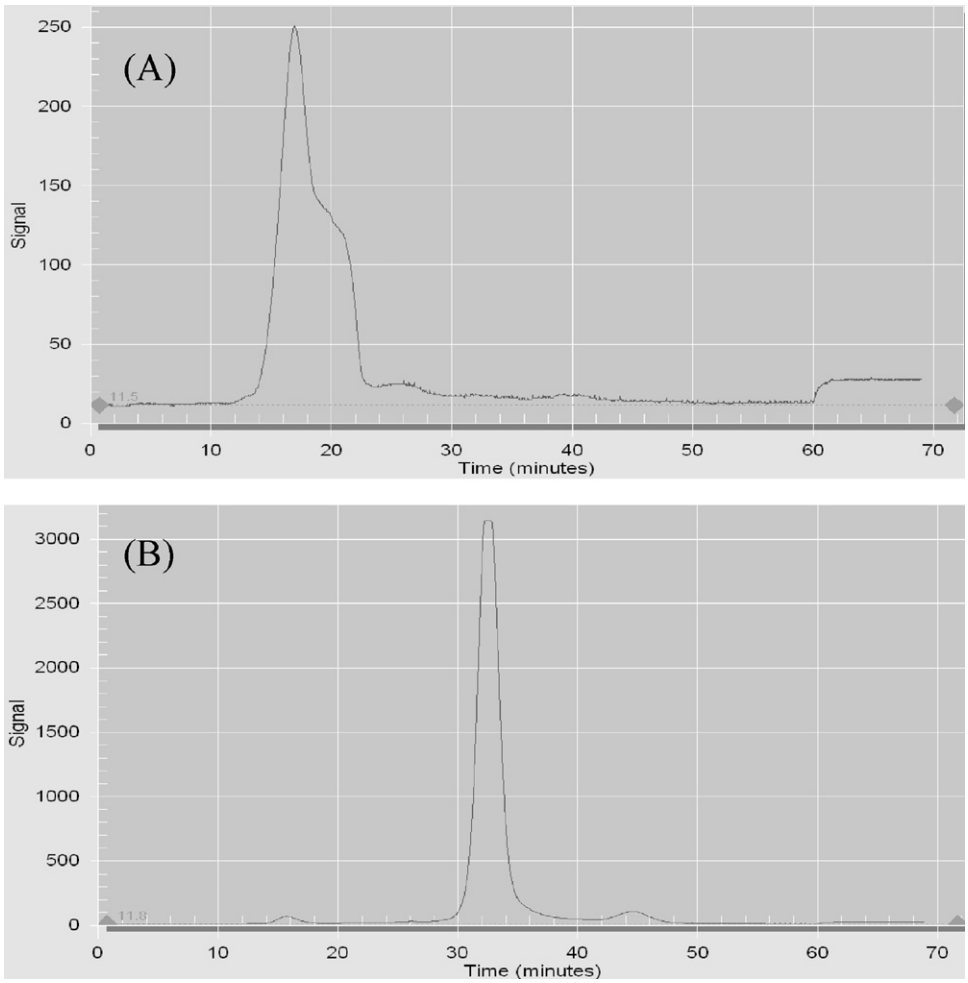

Fig. 5. The eluting chromatogram of blank pig adipose sample (A) and analytes spiked into the pig adipose sample (B) from the GPC.

were selected for each compound and were identified based on their retention times (t_R), characteristic ions in mass spectra and the intensity ratio of the two qualitative ions.

The GC column temperature was optimised to improve both the elution time and chromatographic resolution of the adipose extracts, even though the MS/MS detection allowed for the resolution of chromatographically co-eluted peaks. After a thorough examination of the peak distribution in the chromatogram, the run was divided into several retention time windows so that no more than 20 MRM transitions were used.

3.4. Method validation

To confirm that it was suitable for practical applications, the optimised method was subjected to a validation process and showed no interference in the retention time (t_R) region of the tested substances. The linearity, sensitivity, recovery and precision of the developed analytical approach were evaluated using pig fat.

The fortification concentration that yielded a signal-to-noise ratio (S/N) ≥ 3 for each chemical was defined as its LOD for the developed method, and the fortification concentration that gave an S/N ≥ 10 was defined as the LOQ. The LODs and LOQs for the 284 chemicals are given in Table 1. The matrix-matched standard analyte solutions were injected into the GC–MS/MS system. All of the analytes were found to be linear, with an $r^2 \geq 0.99$ between the LOQ and 100 × LOQ for groups A, B, C and D and between the LOQ and 20 × LOQ for group E. The mixed standard solutions were added to pig fat samples free of any analytical target residues to obtain concentration levels at the LOQ, 2 × LOQ and 4 × LOQ levels. The analytical substances were thoroughly absorbed into the fat sample before extraction by equilibrating for 8 h after fortification with the appropriate standard solution. The recoveries and precisions obtained for the three fortification levels are listed in Table 2. It was concluded that most of the recoveries for these chemicals were in the range of 70–120%. However, the recoveries of some PCBs with a higher number of chlorines were lower, in the range of 40–60%, and the recoveries of several PAHs and PAEs were in the range of 120–130%. These recoveries could also be acceptable if the calculated concentrations were adjusted accordingly.

3.5. Application of the analysis to human adipose tissue

The established method was used to successfully quantify the concentrations of the 284 contaminants in human adipose tissue samples from 633 individuals from three regions in Southeast China. The mean age of the studied subjects was 43.1 years old, ranging from 14 to 91 years of age (with 18.8% of 14–25 years, 29.4% of 26–45 years and 51.8% of 46–91 years old). The gender proportion of the studied subjects was approximately 1:1. The human adipose tissue samples from patient abdominal operations were collected from the corresponding hospital of the three studied regions. The results showed that the organochlorine pesticides, which included 2,4′-DDD, 2,4′-DDE, 2,4′-DDT, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, α-HCH, β-HCH, γ-HCH, δ-HCH, hexachlorobenzene (HCB) and mirex, were

Table 2
The method validation result of 284 analytes ($n = 6$).

Number	Name	LOD (μg/kg)	LOQ (μg/kg)	LOQ (μg/kg)		2LOQ (μg/kg)		4LOQ (μg/kg)	
				AVE (%)	RSD (%)	AVE (%)	RSD (%)	AVE (%)	RSD (%)
Group A									
1	PCB 001	4.00	12.0	102	4.24	86.0	2.31	102	3.46
2	PCB 004	4.00	12.0	124	12.1	99.0	8.82	109	6.81
3	PCB 008	4.00	12.0	97.7	4.27	86.6	6.30	101	3.43
4	PCB 019	4.00	12.0	95.9	5.80	91.6	2.29	99.0	3.59
5	PCB 012	4.00	12.0	93.8	3.96	86.7	5.89	92.8	4.17
6	PCB 027	4.00	12.0	95.5	5.95	87.1	4.09	93.8	3.75
7	PCB 016	4.00	12.0	101	3.07	88.7	3.15	98.3	3.44
8	PCB 025	4.00	12.0	84.6	3.76	81.4	2.51	86.5	4.31
9	PCB 021	4.00	12.0	88.9	2.90	81.6	2.25	89.6	3.55
10	PCB 020	4.00	12.0	94.3	7.66	85.1	2.37	92.4	4.03
11	PCB 036	4.00	12.0	78.0	6.75	75.5	3.49	84.8	4.82
12	PCB 043	4.00	12.0	87.7	4.29	85.1	1.69	89.4	4.27
13	PCB 065	4.00	12.0	90.0	5.94	81.1	2.52	94.1	3.95
14	PCB 104	4.00	12.0	85.3	4.10	78.3	6.05	83.3	5.43
15	PCB 072	4.00	12.0	77.6	7.05	74.8	2.35	79.4	3.32
16	PCB 103	4.00	12.0	86.3	6.15	75.0	3.88	81.7	5.37
17	PCB 041	4.00	12.0	88.6	4.47	82.3	3.33	90.1	4.06
18	PCB 067	4.00	12.0	77.9	5.16	74.4	2.36	79.7	3.00
19	PCB 040	4.00	12.0	80.6	6.84	70.0	3.41	97.7	4.81
20	PCB 074	4.00	12.0	80.8	6.98	70.0	3.36	79.6	4.02
21	PCB 102	4.00	12.0	80.7	6.00	74.1	5.95	80.2	3.11
22	PCB 095	4.00	12.0	91.6	6.33	76.9	4.97	87.8	4.40
23	PCB 092	6.70	20.0	82.5	8.36	77.4	3.13	78.6	5.54
24	PCB 099	4.00	12.0	78.7	9.20	69.1	4.71	78.5	4.25
25	PCB 084	4.00	12.0	96.6	4.17	81.2	3.48	90.6	2.82
26	PCB 109	4.00	12.0	76.8	4.02	78.6	3.58	82.3	3.39
27	PCB 083	6.70	20.0	86.9	8.09	73.3	8.74	82.7	6.67
28	PCB 086	4.00	12.0	78.6	4.61	75.6	3.97	80.9	3.42
29	PCB 125	4.00	12.0	78.2	4.33	71.2	4.44	82.3	2.58
30	PCB 087	4.00	12.0	77.5	3.73	77.8	3.42	81.4	3.87
31	PCB 110	4.00	12.0	79.7	6.40	73.8	2.33	84.6	2.60
32	PCB 135	4.00	12.0	79.4	5.97	70.1	4.96	78.8	3.21
33	PCB 124	4.00	12.0	70.8	3.44	64.0	3.72	70.2	4.45
34	PCB 123	4.00	12.0	67.4	6.85	61.4	4.34	63.7	4.42
35	PCB 118	4.00	12.0	71.5	5.77	63.1	2.48	70.0	4.10
36	PCB 134	4.00	12.0	84.0	3.23	73.3	4.26	83.2	3.25
37	PCB 114	6.70	20.0	71.4	5.61	66.9	4.87	73.7	4.39
38	PCB 168	4.00	12.0	69.4	5.10	60.9	8.24	66.9	5.49
39	PCB 127	4.00	12.0	64.2	5.02	57.8	2.55	64.7	3.97
40	PCB 137	4.00	12.0	66.0	5.25	62.1	4.03	68.0	5.25
41	PCB 163	4.00	12.0	71.7	4.96	67.3	3.33	75.0	3.68
42	PCB 178	4.00	12.0	64.9	3.51	60.9	3.04	68.3	4.21
43	PCB 187	4.00	12.0	66.7	5.59	62.8	2.50	64.1	3.54
44	PCB 162	4.00	12.0	61.9	5.29	54.9	2.52	62.8	4.88
45	PCB 202	4.00	12.0	56.0	5.82	52.9	1.98	59.4	4.95
46	PCB 204	4.00	12.0	46.9	5.09	40.6	3.73	46.8	4.97
47	PCB 197	4.00	12.0	49.6	3.87	45.8	2.01	49.6	3.57
48	PCB 192	4.00	12.0	63.8	8.48	52.4	2.67	62.4	3.45
49	PCB 193	4.00	12.0	62.7	6.84	53.3	3.56	63.7	5.96
50	PCB 190	4.00	12.0	61.8	6.06	57.7	4.58	63.5	3.75
51	PCB 169	4.00	12.0	57.3	6.84	52.5	4.49	61.3	4.08
52	PCB 195	4.00	12.0	54.1	4.57	49.7	4.07	57.2	4.49
53	PCB 206	4.00	12.0	42.8	5.05	41.5	7.12	44.9	5.56
54	PCB 209	4.00	12.0	35.3	14.9	32.1	6.54	34.5	5.84
Group B									
55	PCB 002	4.00	12.0	86.2	6.32	89.6	2.71	82.8	1.53
56	PCB 007	4.00	12.0	83.8	4.50	89.7	1.50	85.1	2.35
57	PCB 005	4.00	12.0	88.5	4.97	94.6	2.34	87.2	2.45
58	PCB 011	4.00	12.0	90.0	4.78	91.0	3.40	84.3	2.55
59	PCB 013	6.70	20.0	88.8	15.7	89.7	4.82	84.1	2.05
60	PCB 032	4.00	12.0	89.9	4.16	93.9	1.37	93.1	2.12
61	PCB 029	4.00	12.0	80.4	9.71	88.8	1.16	88.2	2.79
62	PCB 050	4.00	12.0	96.3	4.73	92.3	3.93	91.7	1.81
63	PCB 053	4.00	12.0	89.0	4.31	104.1	3.62	90.7	4.68
64	PCB 022	4.00	12.0	87.4	4.95	94.1	2.35	90.2	1.98
65	PCB 073	4.00	12.0	82.2	4.68	88.4	3.77	85.5	2.56
66	PCB 039	4.00	12.0	82.0	7.64	84.3	4.10	77.1	2.31
67	PCB 062	4.00	12.0	81.8	3.80	94.1	1.95	86.7	2.18
68	PCB 038	6.70	20.0	83.4	6.29	86.4	3.21	81.0	1.70
69	PCB 035	4.00	12.0	84.1	6.14	87.7	2.59	82.7	3.39
70	PCB 064	4.00	12.0	87.3	6.20	89.6	2.47	82.7	1.47
71	PCB 037	4.00	12.0	82.2	4.24	87.5	2.76	80.0	1.31
72	PCB 080	4.00	12.0	76.1	5.75	81.9	2.32	77.8	1.41

Table 2 (*Continued*)

Number	Name	LOD (μg/kg)	LOQ (μg/kg)	LOQ (μg/kg)		2LOQ (μg/kg)		4LOQ (μg/kg)	
				AVE (%)	RSD (%)	AVE (%)	RSD (%)	AVE (%)	RSD (%)
73	PCB 058	4.00	12.0	81.5	4.52	81.8	3.70	76.5	2.50
74	PCB 121	6.70	20.0	66.7	6.28	77.6	3.21	67.8	3.09
75	PCB 093	4.00	12.0	84.7	6.62	90.8	4.05	85.6	1.30
76	PCB 066	4.00	12.0	76.1	6.20	78.3	2.27	71.6	2.10
77	PCB 090	4.00	12.0	72.0	8.86	78.8	1.79	71.7	2.20
78	PCB 113	4.00	12.0	76.8	8.87	82.9	6.35	70.1	3.85
79	PCB 089	4.00	12.0	80.3	6.60	96.2	3.26	88.4	1.66
80	PCB 152	4.00	12.0	79.2	6.01	81.8	3.67	79.0	1.60
81	PCB 145	4.00	12.0	79.8	8.71	83.4	4.23	75.3	2.70
82	PCB 115	4.00	12.0	77.3	4.14	82.3	3.08	76.0	2.68
83	PCB 154	4.00	12.0	62.8	6.13	69.4	3.30	64.6	3.22
84	PCB 085	4.00	12.0	80.0	5.85	86.1	2.50	76.3	2.08
85	PCB 151	4.00	12.0	75.8	8.55	83.6	3.31	75.1	3.87
86	PCB 139	4.00	12.0	70.1	6.33	70.1	2.94	70.9	1.53
87	PCB 140	4.00	12.0	69.6	6.32	74.1	3.65	68.5	2.62
88	PCB 107	4.00	12.0	70.8	4.65	67.0	5.14	70.4	3.27
89	PCB 143	4.00	12.0	79.4	7.87	75.9	4.89	71.1	3.08
90	PCB 142	4.00	12.0	82.5	9.84	78.7	6.24	76.2	5.28
91	PCB 146	4.00	12.0	67.3	5.99	72.7	2.74	63.7	2.73
92	PCB 122	4.00	12.0	76.1	9.67	73.7	3.42	68.4	1.97
93	PCB 141	4.00	12.0	66.8	6.30	72.6	4.91	61.9	2.11
94	PCB 130	4.00	12.0	74.6	13.1	78.7	7.10	64.1	8.18
95	PCB 138	4.00	12.0	68.8	7.98	72.8	4.80	66.4	1.62
96	PCB 175	4.00	12.0	60.6	5.67	70.8	4.95	58.5	3.11
97	PCB 183	4.00	12.0	62.9	9.56	65.4	6.48	58.4	3.87
98	PCB 166	4.00	12.0	73.2	6.60	80.2	3.25	70.7	1.91
99	PCB 128	4.00	12.0	65.1	7.04	76.0	5.04	70.6	2.80
100	PCB 200	4.00	12.0	52.4	7.23	54.9	4.44	49.3	1.70
101	PCB 173	4.00	12.0	73.9	6.98	76.9	5.42	69.2	1.59
102	PCB 157	4.00	12.0	60.9	7.37	65.3	1.97	58.6	2.34
103	PCB 191	4.00	12.0	56.0	7.42	58.3	4.14	53.5	2.59
104	PCB 203	4.00	12.0	53.4	12.5	56.7	4.90	47.2	1.60
105	PCB 208	4.00	12.0	41.8	7.08	46.5	2.22	41.8	2.88
106	PCB 194	6.70	20.0	50.2	9.19	50.1	6.01	46.7	1.89
Group C									
107	PCB 003	4.00	12.0	97.5	2.56	89.7	3.95	97.7	2.24
108	PCB 009	4.00	12.0	91.8	1.88	96.9	4.88	97.8	2.54
109	PCB 014	4.00	12.0	91.7	3.92	90.3	5.61	95.4	1.99
110	PCB 018	4.00	12.0	110	4.61	92.6	2.66	98.0	1.89
111	PCB 024	4.00	12.0	99.8	6.13	101.2	3.80	98.8	3.34
112	PCB 023	4.00	12.0	91.3	6.09	84.4	3.27	94.5	2.67
113	PCB 054	4.00	12.0	106	3.87	96.1	3.96	103	2.15
114	PCB 031	4.00	12.0	88.0	8.27	90.1	9.87	92.1	2.31
115	PCB 033	4.00	12.0	96.5	3.75	90.9	4.24	95.2	2.55
116	PCB 069	4.00	12.0	98.4	6.14	89.9	2.37	92.2	1.45
117	PCB 075	4.00	12.0	98.7	10.62	81.3	5.15	89.9	1.83
118	PCB 046	4.00	12.0	102	6.35	82.4	3.66	94.4	1.31
119	PCB 047	4.00	12.0	95.8	2.92	92.6	1.39	95.3	1.53
120	PCB 044	4.00	12.0	107	7.69	96.6	5.67	107	8.70
121	PCB 042	4.00	12.0	101	5.97	86.0	4.77	92.8	2.75
122	PCB 071	4.00	12.0	99.5	10.1	90.4	7.76	97.3	3.86
123	PCB 096	4.00	12.0	105	5.04	93.7	4.42	98.2	2.33
124	PCB 088	4.00	12.0	100	9.60	88.9	3.41	96.2	3.27
125	PCB 094	4.00	12.0	101	4.60	88.8	0.92	91.6	2.63
126	PCB 098	4.00	12.0	97.5	5.10	85.8	4.54	89.6	2.64
127	PCB 076	4.00	12.0	88.1	8.04	77.1	2.62	85.3	1.47
128	PCB 091	4.00	12.0	105	6.91	80.9	5.98	95.9	3.61
129	PCB 101	4.00	12.0	85.0	9.40	75.6	6.01	82.8	1.57
130	PCB 056	4.00	12.0	97.8	9.44	76.9	6.44	90.0	1.16
131	PCB 119	6.70	20.0	86.3	11.6	68.4	4.34	78.1	2.36
132	PCB 079	4.00	12.0	82.7	11.4	69.7	5.12	83.0	1.63
133	PCB 116	4.00	12.0	93.1	11.8	74.7	5.46	88.5	3.23
134	PCB 117	4.00	12.0	91.7	6.79	76.1	4.11	87.4	1.48
135	PCB 078	4.00	12.0	91.9	9.55	72.8	3.20	81.0	3.13
136	PCB 136	4.00	12.0	92.7	6.80	80.7	3.04	92.3	2.37
137	PCB 144	4.00	12.0	80.6	7.59	75.9	5.84	81.0	1.94
138	PCB 077	4.00	12.0	91.2	9.19	71.7	5.92	86.8	3.19
139	PCB 149	4.00	12.0	86.0	5.49	74.2	2.58	80.7	3.13
140	PCB 188	4.00	12.0	71.4	10.2	61.0	2.81	66.2	3.91
141	PCB 133	4.00	12.0	78.3	8.88	67.7	8.11	77.2	3.88
142	PCB 165	4.00	12.0	85.8	9.80	71.8	4.16	84.7	3.24
143	PCB 161	4.00	12.0	74.6	8.42	64.3	3.04	73.1	3.85
144	PCB 132	4.00	12.0	90.2	7.39	72.3	3.37	87.1	2.35
145	PCB 105	4.00	12.0	82.8	10.5	69.6	4.35	81.4	1.76
146	PCB 186	4.00	12.0	77.7	8.01	67.8	3.48	76.0	2.87

Table 2 (*Continued*)

Number	Name	LOD (μg/kg)	LOQ (μg/kg)	LOQ (μg/kg)		2LOQ (μg/kg)		4LOQ (μg/kg)	
				AVE (%)	RSD (%)	AVE (%)	RSD (%)	AVE (%)	RSD (%)
147	PCB 158	4.00	12.0	80.3	14.0	62.3	7.76	72.6	4.14
148	PCB 182	4.00	12.0	69.4	12.8	51.8	5.40	62.4	3.92
149	PCB 159	4.00	12.0	69.1	12.6	60.6	3.87	67.2	3.17
150	PCB 167	6.70	20.0	66.3	8.78	57.9	3.91	62.6	3.40
151	PCB 174	4.00	12.0	69.9	9.74	61.2	6.82	71.4	3.39
152	PCB 177	4.00	12.0	81.3	10.7	59.5	6.16	72.6	3.58
153	PCB 156	4.00	12.0	76.4	11.6	58.7	5.14	70.8	2.98
154	PCB 180	4.00	12.0	46.0	20.2	38.5	20.1	56.5	2.83
155	PCB 198	4.00	12.0	63.7	11.3	49.0	8.12	57.6	4.22
156	PCB 196	4.00	12.0	56.9	10.7	46.7	6.81	52.0	3.13
157	PCB 207	4.00	12.0	49.7	16.5	36.2	9.05	43.4	2.91
158	PCB 205	4.00	12.0	63.7	14.7	44.9	8.84	53.4	2.44
Group D									
159	PCB 010	4.00	12.0	114	5.70	88.0	5.89	88.7	4.72
160	PCB 006	6.70	20.0	109	3.60	87.1	5.69	83.8	4.01
161	PCB 030	4.00	12.0	98.6	5.12	82.5	6.31	81.0	5.84
162	PCB 017	4.00	12.0	94.3	4.22	88.8	6.72	87.2	5.45
163	PCB 015	4.00	12.0	97.8	6.20	83.7	7.18	81.8	5.74
164	PCB 034	4.00	12.0	91.4	5.50	77.0	6.61	76.8	6.94
165	PCB 026	4.00	12.0	94.7	5.42	78.9	6.21	82.4	5.08
166	PCB 028	4.00	12.0	87.3	4.32	84.4	10.40	78.0	6.82
167	PCB 051	4.00	12.0	99.5	3.85	85.4	5.56	86.9	5.33
168	PCB 045	4.00	12.0	102	4.17	92.7	6.84	90.9	4.61
169	PCB 052	4.00	12.0	93.5	4.91	80.4	7.57	87.1	4.37
170	PCB 049	4.00	12.0	89.3	8.81	78.5	6.39	88.8	4.86
171	PCB 048	4.00	12.0	94.0	6.11	83.8	7.33	77.8	6.85
172	PCB 059	4.00	12.0	100	5.13	89.1	7.48	79.5	4.61
173	PCB 068	4.00	12.0	79.7	5.34	73.9	5.48	69.3	6.10
174	PCB 100	4.00	12.0	89.0	6.09	76.1	8.51	71.7	3.59
175	PCB 057	4.00	12.0	87.3	4.08	76.0	4.02	71.6	5.18
176	PCB 063	4.00	12.0	93.3	14.1	81.2	5.93	74.5	2.10
177	PCB 061	4.00	12.0	88.8	6.52	75.2	6.28	75.0	3.68
178	PCB 155	4.00	12.0	70.3	5.56	64.1	5.82	63.1	4.47
179	PCB 070	4.00	12.0	87.6	5.83	75.8	4.77	73.3	5.39
180	PCB 055	4.00	12.0	87.6	9.01	81.2	5.38	75.8	5.23
181	PCB 060	4.00	12.0	88.8	7.09	80.6	6.32	73.3	4.23
182	PCB 150	4.00	12.0	82.3	9.08	75.2	7.90	71.5	5.27
183	PCB 112	4.00	12.0	88.7	5.67	79.5	5.70	76.8	4.30
184	PCB 148	4.00	12.0	72.3	6.79	65.7	7.10	66.2	5.05
185	PCB 111	4.00	12.0	77.0	7.12	68.7	8.60	60.2	4.01
186	PCB 097	4.00	12.0	93.2	5.80	75.5	13.6	67.4	12.6
187	PCB 120	4.00	12.0	76.0	6.91	62.1	8.94	57.1	4.39
188	PCB 081	4.00	12.0	72.8	9.43	70.2	6.86	60.8	5.74
189	PCB 147	4.00	12.0	74.0	8.48	64.0	10.4	51.2	10.70
190	PCB 082	4.00	12.0	84.8	4.80	72.4	3.05	66.8	5.17
191	PCB 108	4.00	12.0	74.0	2.12	60.3	7.42	53.4	5.00
192	PCB 106	6.70	20.0	70.4	3.86	64.2	6.12	60.3	4.90
193	PCB 184	4.00	12.0	59.3	4.17	53.5	6.75	47.7	5.66
194	PCB 131	4.00	12.0	77.6	2.09	70.8	6.03	67.0	5.33
195	PCB 153	6.70	20.0	74.8	4.16	57.5	10.5	54.0	5.23
196	PCB 179	4.00	12.0	79.3	5.24	70.2	7.41	63.7	4.08
197	PCB 176	4.00	12.0	69.9	6.82	65.2	5.24	58.9	4.61
198	PCB 160	4.00	12.0	81.6	9.14	79.9	5.74	65.4	6.16
199	PCB 164	4.00	12.0	76.2	6.50	64.9	7.58	67.5	13.76
200	PCB 129	4.00	12.0	76.3	7.70	69.6	6.92	66.1	7.22
201	PCB 126	4.00	12.0	72.1	8.32	67.5	7.33	58.8	7.19
202	PCB 185	4.00	12.0	74.4	6.64	65.2	6.35	59.3	6.36
203	PCB 181	4.00	12.0	64.1	7.38	59.7	7.96	56.6	5.15
204	PCB 171	4.00	12.0	71.4	9.30	62.5	6.96	58.9	7.06
205	PCB 172	4.00	12.0	65.6	8.27	57.9	7.66	53.9	6.26
206	PCB 199	4.00	12.0	62.2	5.54	54.3	6.38	53.6	6.02
207	PCB 201	4.00	12.0	58.6	11.6	53.2	8.42	52.1	5.51
208	PCB 170	4.00	12.0	63.6	8.71	62.2	9.93	55.4	5.00
209	PCB 189	4.00	12.0	57.7	9.86	49.6	7.26	46.5	7.24
Group E									
210	Naphthalene	1.00	1.90	82.0	18.2	65.1	12.2	64.6	18.4
211	Isoprotuton	127	253	85.9	6.60	103	7.24	87.6	3.91
212	Dichlorvos	5.90	11.8	82.7	10.2	86.8	6.48	88.9	6.55
213	Carbofuron	4.30	8.60	90.9	9.12	101	4.73	109	6.27
214	Methamidophos	85.4	171	124	10.8	101	6.28	94.8	5.59
215	Acenaphthylene	2.20	4.50	123	18.2	123	22.5	91.9	10.2
216	Acenaphthene	4.60	9.10	116	8.48	105	11.3	95.6	8.46
217	Fluorene	6.60	13.2	130	16.7	128	20.4	101	13.5
218	Hexachlorobenzene	2.90	5.80	90.7	4.70	89.9	8.27	91.2	3.91
219	Ethoprophos	1.30	2.60	110	20.1	99.1	10.2	115	12.8

Table 2 (*Continued*)

Number	Name	LOD (μg/kg)	LOQ (μg/kg)	LOQ (μg/kg)		2LOQ (μg/kg)		4LOQ (μg/kg)	
				AVE (%)	RSD (%)	AVE (%)	RSD (%)	AVE (%)	RSD (%)
220	Chlordimeform	5.80	11.6	110	12.6	109	11.6	105	6.50
221	Trifluralin	4.50	9.00	63.5	4.36	66.1	2.70	82.1	2.49
222	α-HCH	4.40	8.70	106	5.18	114	4.62	102	1.60
223	Omethoate	18.2	36.5	82.8	16.1	78.2	8.18	81.0	7.37
224	Anthracene	0.10	0.300	108	21.9	105	19.2	110	16.0
225	Clomazone	2.90	5.80	99.7	6.10	93.6	8.07	113	3.23
226	Diazinon	2.70	5.40	73.5	8.70	95.4	4.81	114	4.13
227	Phenathrene	5.30	10.5	125	20.0	130	20.4	119	16.5
228	γ-HCH	4.30	8.60	94.4	4.02	103	3.82	102	3.86
229	Atrazine	4.00	7.90	82.5	7.40	91.4	5.60	98.6	2.22
230	Simazine	11.8	23.5	91.4	5.72	103	4.06	115	2.93
231	Heptachlor	6.50	13.0	96.7	3.00	112	4.34	114	4.39
232	Pirimicarb	3.10	6.10	93.1	2.78	106	3.31	112	1.79
233	Dimethoate	6.50	13.1	116	5.97	124	11.3	124	3.56
234	Aldrin	4.60	9.10	93.7	18.1	83.0	6.39	104	7.13
235	Alachlor	2.90	5.80	91.9	11.3	110	4.28	118	3.92
236	Prometryne	2.70	5.40	86.9	6.14	94.6	4.83	108	3.05
237	Chlorothalonil	233	466	69.0	19.9	101	20.1	105	20.3
238	Phthalic acid bis-butyl ester	6.60	13.3	134	18.8	88.3	8.52	109	5.00
239	β-HCH	4.50	9.00	90.6	5.27	104	6.59	106	5.60
240	Chlorpyrifos	4.50	9.00	88.8	10.1	89.5	7.00	104	5.98
241	Parathion-methyl	4.30	8.60	80.0	8.72	102	4.87	113	4.70
242	Dicofol	3.40	6.70	86.7	6.37	100	20.1	98.1	2.35
243	Metolachlor	1.10	2.20	94.5	1.52	104	2.03	109	1.43
244	δ-HCH	4.30	8.70	110	6.11	108	7.51	112	4.42
245	Triadimefon	4.80	9.60	85.2	4.48	101	4.29	111	2.78
246	Fluoranthene	3.00	6.10	124	20.1	124	60.7	112	18.4
247	2,4′-DDE	6.70	13.3	90.8	1.89	102	3.65	96.7	2.16
248	Cis-chlordane	6.30	12.5	81.5	5.65	101	5.16	96.3	3.61
249	Phenthoate	0.40	0.900	97.0	2.89	111	6.61	113	4.48
250	Trans-chlordane	6.20	12.4	102	6.36	87.9	6.36	101	3.72
251	Pyrene	5.20	10.5	126	19.6	119	21.1	109	18.3
252	4,4′-DDE	6.60	13.1	94.0	2.29	94.3	2.38	88.0	2.41
253	Butachlor	0.700	1.50	105	20.1	124	9.85	107	7.93
254	Dieldrin	13.2	26.3	95.6	5.93	98.3	9.23	104	3.91
255	2,4′-DDD	2.70	5.40	97.4	1.74	100	3.38	103	7.82
256	Buprofezin	14.5	29.1	112	12.5	106	5.42	104	2.81
257	Endrin	30.0	60.0	98.9	6.49	107	4.52	106	4.06
258	2,4′-DDT	2.10	4.20	87.3	8.19	101	5.48	125	19.9
259	Nithophen	8.10	16.2	104	9.19	97.9	2.65	109	5.80
260	Oxyfluorfen	14.6	29.2	96.3	5.74	90.2	4.73	110	3.88
261	4,4′-DDD	6.60	13.3	95.6	1.66	101	3.10	103	1.90
262	4,4′-DDT	3.00	5.90	98.6	10.0	117	7.90	110	8.00
263	Phthalic acid benzyl butyl ester	6.60	13.1	90.2	20.2	78.7	4.22	98.4	1.89
264	Propargite	128	255	94.6	13.7	107	7.95	103	4.30
265	Tricyclazole	0.700	1.50	92.3	7.38	109	5.79	118	7.81
266	Triazophos	11.4	22.9	106	9.76	107	10.6	102	6.62
267	Mirex	2.80	5.50	75.3	4.39	73.9	3.28	77.8	17.9
268	Benzo(a)anthrancene	2.00	4.00	119	20.3	118	20.0	110	18.7
269	Phthalic acid bis-2-ethylhexyl ester	1.30	2.70	123	13.9	137	20.2	125	19.9
270	Amitraz	1.60	3.10	77.7	5.55	77.0	3.63	88.8	2.41
271	Lamba-cyhalothrin	6.40	12.8	45.7	12.9	45.3	6.84	44.8	5.70
272	Pyridaben	6.70	13.3	96.1	1.12	101	2.77	101	2.71
273	Benzo(b)fluoranthene	0.100	0.200	121	19.9	112	20.3	109	20.3
274	Benzo(k)fluoranthene	0.200	0.400	128	19.4	111	20.2	110	20.4
275	Cyfluthrin	8.70	17.5	92.4	8.89	125	14.2	117	5.99
276	Cypermethrin	18.5	37.1	101	3.57	116	5.50	104	4.90
277	Benzo(a)pyrene	1.80	3.50	109	20.3	117	19.4	108	13.3
278	Acetamiprid	27.3	54.6	80.9	7.75	91.5	4.81	103	4.50
279	Fenvalerate-1	29.0	58.1	100	6.60	102	4.28	113	7.11
280	Fenvalerate-2	29.0	58.1	103	9.05	107	7.18	113	7.82
281	Deltamethrin	24.2	48.4	128	20.2	120	8.63	125	16.1
282	Indeno(1,2,3-cd)pyrene	2.20	4.40	129	20.0	122	20.0	110	19.7
283	Dibenzo(a,h)anthracene	2.20	4.40	127	19.7	112	20.0	85.6	7.02
284	Benzo(g,h,i)peryene	2.20	4.40	122	20.1	126	20.1	120	20.2

frequently detected. Other pesticides with lower detection frequencies were dicofol, methamidophos and chlordimeform. The mean total levels for DDT, HCH, HCB, mirex, methamidophos, chlordimeform and dicofol in the three regions were between 0.969 and 3.710 mg/kg, 0.191 and 0.428 mg/kg, 0.0163 and 0.0394 mg/kg, 0.00149 and 0.00255 mg/kg, 0.00100 and 0.0547 mg/kg, 0.00291 and 0.00906 mg/kg and 0.00319 and 0.00704 mg/kg, respectively. PAHs and PAEs were also frequently detected with mean values of detection in the three regions between 0.0416 and 0.0988 mg/kg and 0.0398 and 0.333 mg/kg, respectively. The detection frequency and level for PCBs were relatively low with mean values in the three regions between 0.00151 and 0.00365 mg/kg. The chromatograms of representative detected pollutants in human adipose tissue were seen in Fig. 6. The ability of this method to detect substances from

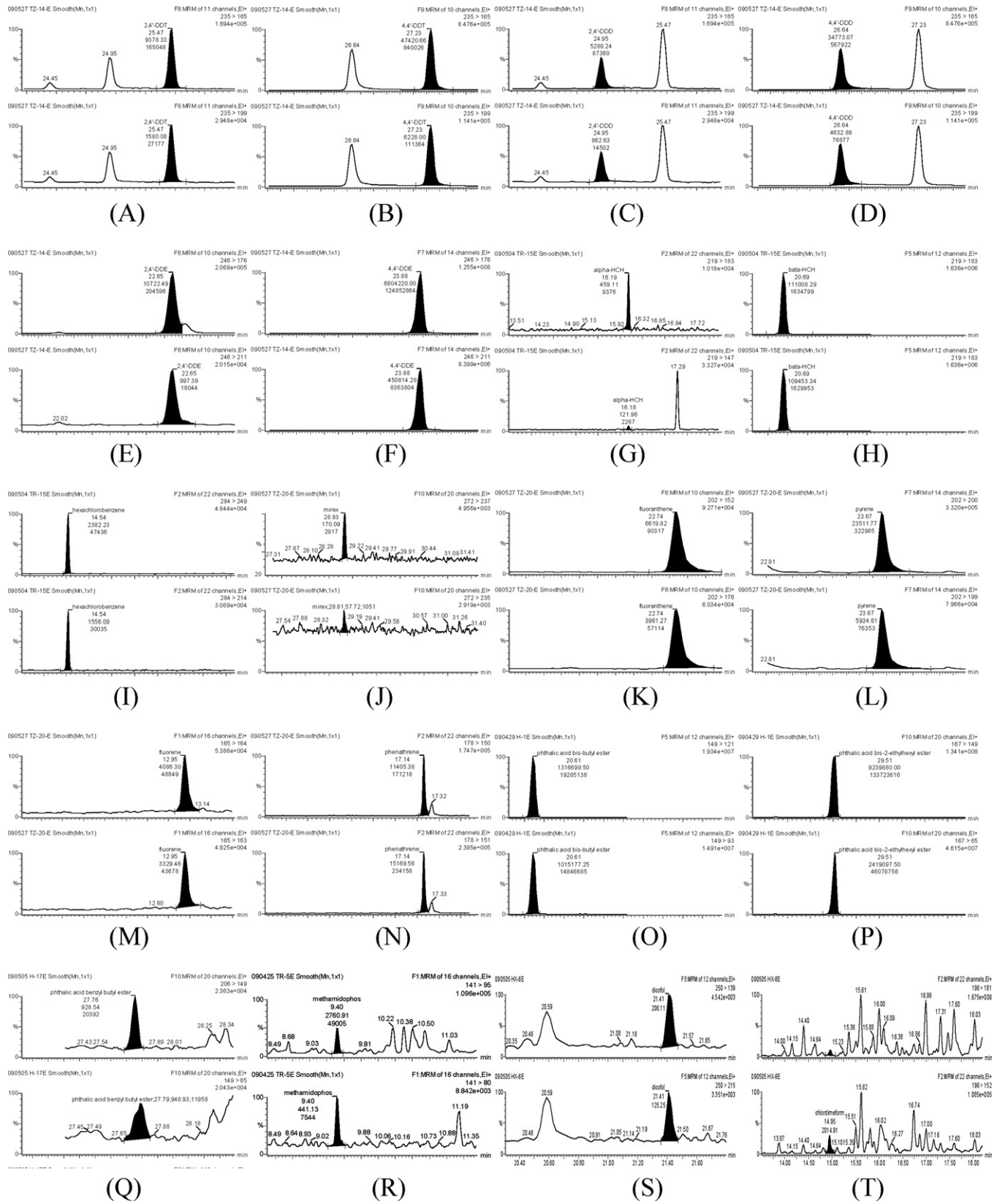

Fig. 6. The chromatograms of representative detected pollutants in human adipose tissue ((A) 2,4′-DDT; (B) 4,4′-DDT; (C) 2,4′-DDD; (D) 4,4′-DDD; (E) 2,4′-DDE; (F) 4,4′-DDE; (G) α-HCH; (H) β-HCH; (I) HCB; (J) mirex; (K) fluoranthene; (L) pyrene; (M) fluorene; (N) phenathrene; (O) phthalic acid bis-butyl ester; (P) phthalic acid bis-2-ethylhexyl ester; (Q) phthalic acid benzyl butyl ester; (R) methamidophos; (S) dicofol; and (T) chlordimeform).

a diverse range of classes, including pesticides, PAHs, PAEs and PCBs, demonstrates the versatility and sensitivity of the proposed method for the determination of contaminants in human adipose samples.

4. Conclusion

The method developed in this study for determining various contaminants, including 57 pesticides, 15 PAHs, 209 PCBs and 3 PAEs, in adipose tissue samples was simple, efficient and reliable. The method performance was satisfactory, with results meeting the validation criteria. This method has been successfully used for the analysis of contaminants in adipose tissue samples. It was concluded that this method provided an efficient tool for evaluating the extent of exposure by measuring the organic contaminants in human adipose tissue.

Acknowledgment

The authors are very grateful for the financial support from the 2008 Commonweal and Environmental protection project for the Ministry of Environmental Protection of the People's Republic of China (MEP) grant "Bioconcentration of Toxic Hazardous Substances in body adipose tissue and risk analysis on human health" (200809102), "333 High-level Talent Cultivation Project" research funding from the Jiangsu Province "Research on human health risk assessment of pesticides" and the 2011 Commonweal and Environmental protection project for the MEP grant "The health risk assessment and management technology of veterinary medicine" (201109038). We acknowledge Daoji Cai and Guofang Pang, both academicians of the China Engineering Academy, for their strong support of this project.

References

[1] J.A. Hogsette, P.G., Koehler, P.E. Kaufman, http://edis.ifas.ufl.edu/IG128, 2006.
[2] T. Heberer, Toxicol. Lett. 131 (2002) 5.
[3] P. Wang, S.L. Wang, C.Q. Fan, Chemosphere 72 (2008) 1567.
[4] P.B. Hoyer, Biochem. Pharmacol. 62 (2001) 1557.
[5] T. Fukuwatari, Y. Suzuki, E. Sugimoto, K. Shibata, Biosci. Biotechnol. Biochem. 66 (2002) 705.
[6] R. McKee, J. Butala, R. David, G. Gan, Reprod. Toxicol. 18 (2004) 1.
[7] P.C. Erkuden, M.L.L. Victor, G.P. Abelardo, G.M. Eduardo, J. Chromatogr. A 1170 (2007) 82.
[8] G. Fernando, L. Raul, E. Arsenio, M. Esmeralda, V. Asunción, A. Pilar, Chemosphere 76 (2009) 1533.
[9] S.U. Barbara, Environ. Toxicol. Pharmacol. 25 (2008) 131.
[10] S.D. Saeger, H. Sergeant, M. Piette, N. Bruneel, W.V.D. Voorde, C.V. Peteghem, Chemosphere 58 (2005) 953.
[11] G.Q. Chen, P.Y. Cao, R.J. Liu, Food Chem. 125 (2011) 1406.
[12] S.L. Song, X.D. Ma, C.J. Li, Food Control 18 (2007) 448.
[13] J. Li, H.F. Zhang, Y.P. Shi, Food Chem. 127 (2011) 784.
[14] G. Wu, X.X. Bao, S.H. Zhao, J.J. Wu, A.L. Han, Q.F. Ye, Food Chem. 126 (2011) 646.
[15] N. Valeria, D. Daniela, P. Carmen, C. Diego, J. Chromatogr. A 1217 (2010) 4996.
[16] Y. Pico, D. Barcelo, Trends Anal. Chem. 27 (2008) 821.
[17] A.K. Malik, C. Blasco, Y. Pico, J. Chromatogr. A. 1217 (2010) 4018.