Determination of PCBs in tetrachlorinated quinone using gas chromatography with electron capture detection

Xin-Hui Bi, Xiao-Bai Xu *, Ming-Hui Zheng, Qing-Yu Meng, Shan Fu

Research Center for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China

Received 9 September 1999; received in revised form 2 February 2000; accepted 10 February 2000

Abstract

A simple, sensitive method for determining polychlorinated biphenyl (PCB) congeners in industrial product 2,3,5,6-tetrachloro-1,4-benzoquinone with GC/ECD detection has been developed. The method based on liquid–liquid extraction from tetrachlorinated quinone dissolved in *N,N*-dimethylformamide was found to be efficient for the determination of the levels of the investigated pollutants. A series of extraction and purification steps were designed for the sample pretreatment. The congener specific averages of recoveries were 82–96% for Aroclor 1242 and 1254 at a total spiking level of ca. $0.4 \mu\text{g g}^{-1}$ sample. The reproducibilities of replicate determinations of different congeners were typically 5–19% except one with the average 13% R.S.D. ($n = 3$). This method was applied to evaluate the background levels of PCBs in tetrachloro-1,4-benzoquinone, of which the corresponding PCB levels varied from 0.014 to $1.5 \mu\text{g g}^{-1}$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PCBs; 2,3,5,6-Tetrachloro-1,4-benzoquinone; Gas chromatography

1. Introduction

Polychlorinated biphenyls (PCBs) are a group of stable, persistent, lipophilic contamination compounds, which occur widely in many media and organisms including human [1–3], as they have been widely used as dielectric and heat transfer fluids, plasticizers, wax extenders and flame retardants [4]. However on account of their known potential toxicity, their industrial use in the US has been restricted since the 1970s [5], and

PCBs have been included in the ‘priority pollutants’ listings implemented by the US Environmental Protection Agency (USEPA) and by the European Commission. Now these compounds have also been considered and proposed for inclusion in the priority pollutant list of the State Administration of Environmental Protection (SAEP) in China. For this reason, the level of PCBs in industrial products is being given more attention.

PCBs theoretically consist of 209 congeners that differ significantly in terms of their physico-chemical properties, persistence and their biological activities. Studies of structure-activity relationships suggest the non-*ortho* PCBs such as

* Corresponding author. Tel.: +86-10-62925511 ext. 2157; fax: +86-10-62923563.

E-mail address: xbxuac@bj.col.com.cn (X.-B. Xu)

PCBs 77(34-34), PCBs 126 (345-34) and PCBs 169 (345-345), substituted with chlorine atoms in both *para*- and at least one *meta*-position, and their mono-*ortho* analogues such as 105 (234-34), 118 (245-34), 123 (345-24), 114 (2345-4) and 167 (245-345) have biological properties similar to the well-known 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [4]. Therefore, congener specific analyses of PCBs in environmental samples are popular now.

The vast majority of PCBs of concern to analytical chemists are derived from commercial sources (e.g. Aroclor series and Clophen series). However, PCBs can also be produced as byproducts in a wide variety of chemical processes which contain chlorine and hydrocarbon sources. The byproduct PCBs are usually generated inadvertently and unintentionally. US rules, therefore, not only control the use of commercial mixtures such as contaminated transformer oils, but also impinge on such industrial processes as manufacture of chlorinated benzenes, vinyl chloride, chlorinated solvents (e.g. chloroform), chlorinated alkanes, which could produce PCBs as byproducts [6].

The prepreparations of PCBs from environmental matrices in their analyses have been reported, largely including supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), solid-phase microextraction (SPME) and subcritical water extraction coupled with solid-phase microextraction [7–10] and so on. But relatively less is known for PCBs contamination in commercial and industrial products. Buchta found PCBs contamination in copper phthalocyanine pigments [11]. Rastogi found seven out of 11 printing inks investigated to contain PCBs in concentrations up to 180 ng g⁻¹ [6]. The aim of this study was to develop a method for determination of PCBs and specifically to manifest the existence and magnitudes of PCBs contamination in the industrial product 2,3,5,6-tetrachloro-1,4-benzoquinone (commercial name chloranil).

Chloranil is one of the familiar quinonoids with all the four positions substituted by electron withdrawing chlorine atoms. The structure of the 2,3,5,6-tetrachloro-1,4-benzoquinone is shown in the diagram.

Because of the sufficiently high electron affinity, chloranil is widely used as the electron acceptor in electron donor–acceptor systems. In addition, it may be used as a fungicide in agriculture and a dye intermediate in industry.

2. Experimental

2.1. Chemical and materials

All reagents utilized were of 'analytical reagent' grade. The solvents used were *N,N*-dimethylformamide, dichloromethane, and hexane. They were obtained from Xinguang Chemical Plant and the Beijing Chemical Plant (Beijing, China) and redistilled in an all-glass appliance before use. Aroclor 1242 and 1254 used as the standard reference materials were obtained from Supelco Corporation. Sodium chloride and anhydrous sodium sulfate (from Beijing Shuanghuan Chemical Reagent Plant and Beijing Lihuadian Chemical Plant) were used to minimize water solubility losses and dry the organic phases. Basic aluminum oxide (100–200 mesh, from the Wusi Chemical Plant of Shanghai) was used for cleaning up the samples.

Stock standard solutions of PCBs were prepared by dissolving Aroclors in hexane. A series of working composite standard solutions were prepared by combining an aliquot of each of the stock solutions and diluting the mixture with hexane. These solutions were stored in dark glass bottles at 4°C.

2,3,5,6-Tetrachloro-1, 4-benzoquinone was obtained from a chemical factory in the north of China and stored in a glass bottle at 4°C before analysis.

2.2. Instrument

Congener-specific PCB analysis was performed on a Varian 3740A gas chromatograph (GC) eq-

uipped with ^{63}Ni electron capture detector. The GC was fitted with a SE-54 capillary column ($40\text{ m} \times 0.25\text{ mm}$ I.D. J & W Scientific Inc., USA). The carrier gas was nitrogen at the flow rate of 17.3 cm s^{-1} . A total of $1\text{ }\mu\text{l}$ of sample was injected to the GC with splitless injection. The oven temperature was programmed as follows: the temperature was initially at 50°C , and held for 2 min. After injection, ramped at 4°C min^{-1} to 280°C , and kept for 10 min. The temperatures of the injector and detector were set at 300°C and 350°C , respectively. A WDL-95 workstation (Dalian Inst. Chem. Phys, CAS, China) was utilized to control the system and for acquisition of analytical data.

2.3. Sample preparation

For determination of PCBs, about 5 g of accurately weighed fine powder of industrial tetrachlorinated quinone was dissolved with *N,N*-dimethylformamide. Where necessary, it was heated to help dissolution. The solution was dark brown. After cooling, the extract was transferred to a separatory funnel with 20 ml *N,N*-dimethylformamide, then 50 ml hexane and 100 ml *N,N*-dimethylformamide/2 mol l^{-1} NaOH solution (1:1, v:v) was added to the funnel. After mixing and layering, the lower layer containing interfering co-extractants and residual 2,3,5,6-tetrachloro-1,4-benzoquinone was removed. The upper hexane layer was washed again with 50 ml 2 mol l^{-1} NaOH solution. The procedure was repeated until the NaOH solution layer remained colorless. The extract was then washed with 2% NaCl solution, dried with 15 g anhydrous Na_2SO_4 packed in a $1\text{ cm} \times 10\text{ cm}$ glass column and was transferred to a K.D. apparatus for concentrating to about 1 ml.

A cleanup was done by chromatography on basic aluminum oxide column with a layer of anhydrous Na_2SO_4 . A total of 10 g of basic aluminum oxide was packed in a $1\text{ cm} \times 33\text{ cm}$ glass column with hexane. After the sample was concentrated as described above, it was transferred onto the basic aluminum oxide column. PCBs were eluted from the column with dichloromethane/hexane (v/v, 1/49) in the first 80 ml fraction. The fraction was concentrated in

K.D. apparatus and under a gentle stream of nitrogen to proper volume.

2.4. Calibration

Standard solutions containing Aroclor mixture in hexane were prepared at seven concentration levels in the range of $0.2\text{--}8\text{ mg l}^{-1}$ and analyzed by GC-ECD. The compounds were identified and quantified by comparing their retention values and integrated peak areas with those of known external standards according to the previous analysis [12].

2.5. Recovery and blank studies

The recovery study was carried out by spiking stock solution $1.97\text{--}2.06\text{ }\mu\text{g}$ of Aroclor 1242 and 1254 into the 5 g solid samples analyzed, respectively, and equilibrating for 12 h. Then the samples were prepared as described above. The background-contaminated levels were estimated with pure solvent instead of the sample by the same procedure.

3. Results and discussion

The blank chromatograms contained only a few insignificant peaks from background contaminants that did not interfere with PCB peaks. The identity of background contaminants was not determined and no blank correction of the results was performed.

Recoveries were calculated by dividing the analytical levels (PCB levels in the original sample itself were subtracted) with the spiked levels. In Table 1, the calculated recoveries were listed. The recoveries of the congeners eluted before PCB56/60 were calculated based on Aroclor 1242, and the others were on Aroclor 1254. All of the congeners in the samples were relatively good, with the average recoveries of all congeners ranging from 82 to 96%, which indicated that the proposed procedure was suitable for determining PCBs in the tetrachlorinated quinoine. From Table 1, it can be seen that the recoveries of highly chlorinated biphenyls appeared somewhat better than

those of less chlorinated biphenyls. This can be explained that the higher chlorinated biphenyls have lower volatility and less water solubility and thus lower loss from the concentration and wash steps. R.S.D. obtained were 5–19%, except one, with the average 13%. This demonstrated that the sample purification and analysis procedures were practically reproducible.

In Fig. 1, The GC chromatograms of Aroclor 1242, 1254 and a sample after pretreatment were shown in which pentachloromethyl benzene, hexachlorinated benzene and dichlorinated biphenyls

Table 1

Percent recoveries of polychlorinated biphenyls (PCBs) in the sampled product

IUPAC no.	Run no.			Mean	R.S.D.
	R ₁	R ₂	R ₃		
18/17	96	72	80	83	14.8
16/32	74	73	82	76	6.5
26/25	94	85	69	83	15.3
31/28	105	95	82	94	12.3
33	66	77	82	75	10.9
22	76	82	86	81	6.2
52	77	107	80	88	18.8
49	84	67	64	72	15.0
47/48	53	56	72	60	16.9
44	89	106	89	95	10.4
41/64	80	98	86	88	10.4
74	120	109	110	113	5.4
70	105	109	68	94	24.0
66	81	83	80	77	7.9
56/60	125	88	115	109	17.5
101	91	97	77	88	11.6
99	97	101	80	93	12.0
97	107	116	83	102	16.7
87	97	108	80	95	14.8
85	96	101	82	93	10.6
110	96	100	78	91	12.8
82	99	100	72	90	17.6
108/118/149	101	112	84	99	14.2
146	102	107	83	97	13.0
153	115	117	88	107	15.2
141	82	80	60	74	16.4
137	92	91	70	84	14.7
138	90	95	72	86	14.1
128	105	115	80	100	18.0
177	127	117	129	124	5.2
180	107	92	76	92	9.8
170	119	121	102	114	9.2
Average	95	96	82	91	13

Fig. 1. GC-ECD chromatogram of aroclors (A) (B) and polychlorinated biphenyls (PCBs) (C) extracted from the tetrachlorinated quinone sample.

were confirmed by GC/MS. Because of the complexity of the compounds in industrial products and the low level of pollutant, an attempt was not made to identify other peaks in the GC chromatogram. But it was suggested that this method could also be modified and applied to the quantification of additional components such as PCDD/PCDFs and chlorobenzene if the purification condition is somewhat changed. As a matter of fact, this method developed can be used in the analyses of PCBs in the product with the similar properties as tetrachlorinated quinone.

PCB concentrations were determined by comparing the GC-ECD chromatographic peak areas to those of commercial Aroclor (1242 and 1254) standards preparation. Twenty seven peaks were detected in the samples according to their retention indexes [12], and their levels for these samples and detection limits were listed in Table 2.

Sample no. 1 had a PCB content of 1.53 $\mu\text{g g}^{-1}$, which was significantly higher than those of the other two samples. The no. 3 sample, which

had been treated additionally through recrystallization, was found to have the lowest contamination of PCBs.

4. Conclusion

The method developed in this laboratory has been successfully applied to separate and determine PCB congeners in the industrial product of tetrachlorinated quinone. The average recoveries of 32 congeners in Aroclor 1242 and 1254 were 82–96%. The reproducibilities of replicate determinations of different congeners were typically 5–19% except one with the average 13% R.S.D.

($n = 3$). The sample-preparation procedure seems to be effective in eliminating troublesome compounds and then producing a clean injection solution for GC-ECD analysis. The chromatographic method allowed sensitive determination of PCBs in tetrachlorinated quinone samples at the ng g^{-1} level. The present or similar sample-preparation and analysis protocol might be also applicable to the measurement of other related compounds in tetrachlorinated quinone or to the analysis of other complex systems. Of course, further testing for more samples are definitely helpful to confirm the application of this assay developed in this paper as it has been conducted only on limited product.

Table 2
Polychlorinated biphenyls (PCBs) levels in tetrachlorinated quinone products

IUPAC no.	Congener	Sample concentration ($\mu\text{g g}^{-1}$)			Detection limit (ng g^{-1})
		No. 1	No. 2	No. 3	
7	24	0.61	0.014	0.0039	0.098
19	22'6	0.065	0.0093	ND ^a	0.14
17/18	22'4/22'5	0.26	0.0058	0.0011	0.08
16/32	22'3/24'6	0.029	0.056	0.0012	0.056
26/25	23'5/23'4	0.010	ND	ND	0.072
31/28	24'5/244'	0.19	ND	ND	0.052
33	2'34	0.019	ND	ND	0.067
22	234'	ND	0.00013	ND	0.029
45	22'36	ND	0.0013	ND	0.08
52	22'55'	0.084	0.0051	ND	0.077
49	22'45'	0.020	0.0017	0.0018	0.048
44	22'35'	0.024	0.0045	ND	0.048
37/42	344'/22'34'	0.012	0.0031	0.0011	0.11
41/64	22'34/234'6	0.006	0.00054	0.00025	0.048
40	22'33'	ND	0.0010	0.0013	0.048
74	244'5	0.018	0.00048	ND	0.15
70	23'4'5	0.0077	0.00033	ND	0.086
56/60	233'4'/2344'	0.014	0.00031	ND	0.032
101	22'455'	0.043	0.0012	ND	0.16
99	22'44'5	0.0028	0.00082	ND	0.17
97	22'3'45	ND	ND	0.0017	0.39
87	22'345'	0.036	0.0014	0.00029	0.074
110	233'4'6	ND	0.0012	ND	0.14
82	22'33'4	0.011	0.0011	ND	0.14
108/118/149	233'45'/23'44'5/22'34'5'6	0.053	0.0012	ND	0.16
146	22'34'55'	ND	ND	0.00092	0.12
138	22'344'5'	0.023	0.00066	ND	0.14
Sum		1.5	0.11	0.014	2.7

^a ND, results below the detection limit or not detected.

Acknowledgements

We thank Mr Shi-Qi Lu for his providing the tetrachlorinated quinone samples and Dr Ming-Jun Piao for his helpful discussion. We are also gratefully indebted to Dr H.F. Zou of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian for his providing the WDL-95 workstation. Financial support from Bureau of Resources and Environment (KZ-951-B1-209-02) and Chemistry Branch of Bureau of Basic Study, CAS are gratefully acknowledged.

References

- [1] L.J. Jackson, D.E. Schindler, *Environ. Sci. Technol.* 30 (1996) 1861.
- [2] H. Iwata, S. Tanabe, K. Ueda, R. Tatsukawa, *Environ. Sci. Technol.* 29 (1995) 792.
- [3] S. Safe, *Toxicol. Environ. Chem.* 5 (1982) 153.
- [4] S. Safe, S. Bandiera, T. Sawyer, L. Robertson, L. Safe, A. Parkinson, P.E. Thomas, D.E. Ryan, L.M. Reik, W. Levin, M.A. Denomme, T. Fujita, *Environ. Health Perspect.* 60 (1985) 47.
- [5] WHO, Geneva, *Environmental Health Criteria* 140, Polychlorinated Biphenyls and Terphenyls, 1993.
- [6] M.D. Erickson, *Analytical Chemistry of PCBs*, Second Edition, CRC/Lewis, Boca Raton, FL, 1997, p. 44.
- [7] W.J. Yoo, L.T. Taylor, *J. AOAC Int.* 80 (1997) 1336.
- [8] B. Witter, W. Francke, S. Franke, Hans-D. Knauth, G. Miehl, *Chemosphere* 37 (1998) 63.
- [9] D.W. Potter, J. Pawlitzyn, *Environ. Sci. Technol.* 28 (1994) 298.
- [10] S.B. Hawthorne, C.B. Grabanski, K.J. Hageman, D.J. Miller, *J. Chromatogr. A* 814 (1998) 151.
- [11] R.C. Buchta, H.F. Wyles, C.J. Hensler, F.J. Van Lenten, R.B. Westerberg, L.A. Williams, *J. Chromatogr.* 325 (1985) 456.
- [12] S.G. Chu, X.S. Miao, X.B. Xu, *J. Chromatogr. A* 724 (1996) 392.