



Simultaneous Determination of Organochlorine Pesticides, Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Water by Solid Phase Disk Extraction-Ultrasonic Desorption and GCMS

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Received: 13 January 2014;

Accepted: 7 April 2014;

Published online: 10 January 2015;

AJC-16615

A method was developed for the simultaneous determination of organochlorine pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in water by solid-phase disk extraction-ultrasonic desorption and gas chromatography-mass (GC-MS). The samples were extracted by C18 solid-phase disk extraction, and ultrasonic wave to promote the extraction of object from the solid phase membranes, which realize the simultaneous purification of 17 types organochlorine pesticides, 16 kinds of polycyclic aromatic hydrocarbons and 2 kinds of aroclors. The recoveries of the compounds of this method were 70-130 %, with relative standard deviation below 10 and the detection limit between 0.2 and 1.1 ng/L, which would satisfy the demand of daily water quality analysis.

Keywords: Solid phase disk extraction, Ultrasonic desorption, Organochlorine pesticides, Polycyclic aromatic hydrocarbons, Aroclors.

INTRODUCTION

Residual and persistent organic pollutants in water could be enriched through the biological amplification of aquatic food chain, which are harmful to aquatic organism and human¹⁻³. Accurate and quantitative monitoring the residue levels of persistent organic pollutants in environment is of importance and practical significance to control the condition of water environmental pollution, to protect aquatic organism and the health of human. Organochlorine pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls are persistent organic pollutants with relative high toxicity⁴. These compounds are lipophilic and semivolatile and unbiodegradable, which can exist in environment for a long time. They contact with biosystem including humans through environment medium such as food, water, air and soil *etc.*, and do have the potential to damage ecotope and human health⁵⁻⁸.

At present, the researches about organochlorine pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls mostly focused on two of them and researches about polychlorinated biphenyls are also mostly about several single standards of polychlorinated biphenyls^{5,9-11}. The methods purified, separated and analyzed the residual of organochlorine pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls which in the form of aroclors mixed standards simultaneously were very few. This study developed a method which can simultaneous determine 17 kinds of organochlorine pesticides, 16 kinds of polycyclic aromatic

hydrocarbons and aroclors. This method is easy to handle and practical, with detection limit satisfying the request of daily water quality analysis.

EXPERIMENTAL

TRACE DSQ-II gas chromatography mass spectrometry (U.S. Company Thermo Fisher), solid phase disk extraction element (Germany, CNW Company), C18 disk (F47 mm, U.S. 3M Company), 12 mL brown vial (U.S. Agileng Company), nitrogen evaporator (Tianjin Automatic Science Instrument Co., LTD), constant temperature water bath apparatus, chromatographic column.

Dichloromethane (pesticide residue grade), *n*-hexane (pesticide residue grade), acetone (pesticide residue grade), methanol (pesticide residue grade), ethyl acetate (pesticide residue grade), silica gel (0.065-0.185 mm), neutral alumina (U.S. Fluka Company).

α -BHC, β -BHC, γ -BHC, δ -BHC, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, aldrin, heptachlor, heptachlor epoxide, dieldrin, endrin, hexachlorobenzene, α -endosulfan, β -endosulfan, endrin aldehyde, methoxychlor, 16 polycyclic aromatic hydrocarbons, Phenanthrene-D10, aroclor 1016, aroclor 1260 procured from Supelco.

Choice of column and instrument requirement: Column: HP-5MS quartz capillary column (30m \times 0.25 mm \times 0.25 μ m); carrier gas: high purity helium gas (99.999 %); chromatogram temperature program: initial temperature at 60 $^{\circ}$ C, maintain

1 min; raise temperature at speed of 30 °C per min to 160 °C, maintain for 2 min; 5 °C per min to 280 °C.

Injection port temperature: 280 °C; joint lever temperature: 260 °C; ion source temperature: 230 °C; injection pattern: Splitless injecting samples 1 µL; scanning system: segment selected ion monitoring.

Preparation of sample: Successively activate the disk with 10 mL dichloromethane, 10 mL methanol and pure water. Add 5 mL isopropanol into 1 L water sample, extract the water sample at speed of 150 mL per min through the disk and then pump the disk with vacuum pump for 5 min. Then hyperacoustic elute the disk for about 10 min at 70 °C and under 560 W power conditions and concentrate to about 1 mL with nitrogen blow and after that add 2 mL *n*-hexane to change solvent, repeat 2 times. Add the extracting solution which have changed solvent into *n*-hexane into silica gel-alumina composite column to purify, at last use gas chromatography mass spectrometry to detect.

RESULTS AND DISCUSSION

Optimizing the mass spectrum: In order to improve the sensitivity of the instrument and lower detection limit, this method used selected ion scanning, subdivided the entire analysis process into 10 times, scanning the characteristic ions of the responding target compounds in every period to qualitatively and quantitatively determine it. Since the scanning frequency of characteristic ions was several times higher than conventional selected ions and ignored most of unrelated ions, the noise signal can be weakened and the separating effect of target compounds was relatively good (Fig. 1). Aroclor 1016 and aroclor 1260 can cover almost all polychlorinated biphenyls, the quantification of polychlorinated biphenyls through respective selection of 4 characteristic peaks of aroclor

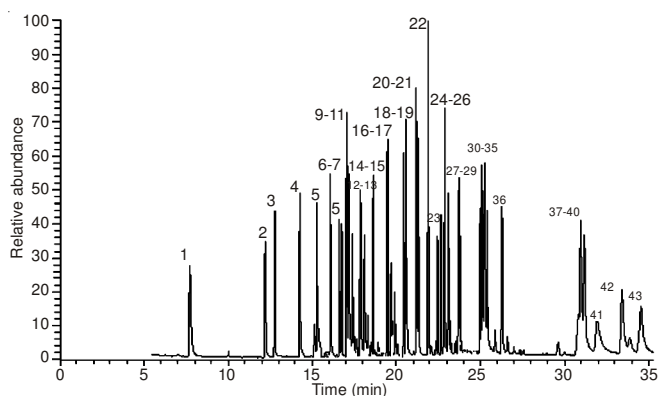


Fig. 1. Selected ions scan (1) Naphthalene; (2) acenaphthene; (3) acenaphthylene; (4) fluorene; (5) α -HCH; (6) hexachlorobenzene; (7) β -HCH; (8) γ -HCH; (9) phenanthrene-D10; (10) phenanthrene; (11) quantitative peak of aroclor1016-1; (12) anthracene; (13) δ -HCH; (14) quantitative peak of aroclor1016-2; (15) heptachlor; (16) quantitative peak of aroclor1016-3; (17) quantitative peak of aroclor1016-4; (18) aldrin; (19) heptachlor epoxide; (20) fluoranthene; (21) pyrene; (22) α -endosulfan; (23) *p,p'*-DDE; (24) dieldrin; (25) quantitative peak of aroclor1260-1; (26) endrin; (27) β -endosulfan; (28) *p,p'*-DDD; (29) endrin aldehyde; (30) quantitative peak of aroclor1260-2; (31) endosulfan-sulfate; (32) *p,p'*-DDT; (33) quantitative peak of aroclor1260-3; (34) benzo(a)anthracene; (35) chrysene; (36) methoxychlor; (37) quantitative peak of aroclor1260-4; (38) benzo[b]fluorathene; (39) benzo[k]fluorathene; (40) benzo(a)pyrene; (41) indeno(1,2,3-cd)pyrene; (42) dibenz[a,h]anthracene; (43) benzo[ghi]pyrene

1016 and aroclor 1260 and the peak height of each selected peak was at least 25 % of the highest peak¹².

Choice of elution solvent: Blank spiked samples were extracted through C18 disk, then used dichloromethane and *n*-hexane/dichloromethane (1:1) as elution solvents to compare the eluted effect, respectively. Experiments showed that when using *n*-hexane/dichloromethane (1:1) as elution solvent, almost all compounds had good recoveries and could also reduce the extract interference, improve signal and noise ratio. For these reasons, *n*-hexane/dichloromethane (1:1) was selected as elution solvent.

Determine elution volume: Compare the influence on recovery of different volume of the elution solvents by respectively adding 1, 2, 3, 5 and 10 mL elution solvents to hyperacoustic elution. Fig. 2 showed that when the volume of elution solvent is 1 mL, the recoveries of each target were relatively low and when the volume is between 2 to 5 mL, the recoveries were well and the difference between different volumes was small. Taking all into consideration, this method determined the elution volume 2.5 mL.

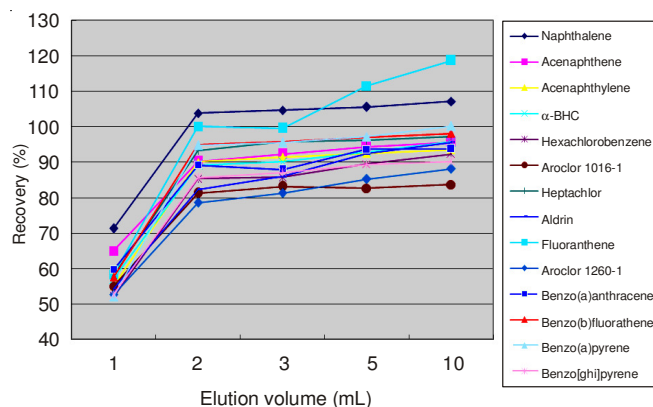


Fig. 2. Elution curve of part of target compounds

Choice of hyperacoustic conditions: The contrast experiment found that when the hyperacoustic time was between 2 to 10 min, as the extension of time, the recoveries gradually increasing and reached maximum at 20 min. The recovery difference of targets was small on hyperacoustic 10 and 20 min. For the above reasons, the method took 10 min as determined the hyperacoustic. The choice of hyperacoustic temperature mainly depends on stability of target compounds and the volatilization of elution solvent *etc.* Because the hyperacoustic elution of this experiment was tested in sealed container, elution solvent could not volatilize. On the other hand, elution effect was good between 50 to 70 °C, so this experiment chose 70 °C as the hyperacoustic temperature. The eluted effect had higher recovery with the increase of ultrasonic power, so this experiment determined the ultrasonic power to be 560 W.

Choice of elution condition of purification column: Added ultrasonic eluent which had changed phase into *n*-hexane into alumina-silica gel composite column to purify. Divided 40 mL *n*-hexane into 5 portions, concentrated each part of eluent into 1 mL through nitrogen blow, tested on the GCMS and then drew elution curve to compare the influence of different volume of elution solvent to recoveries of target compounds (Fig. 3). As the results showed that when used

TABLE-1
THE RECOVERY, RSD AND LIMIT OF DETECTION (LOD)

Compounds	Spiked (µg/L)	Recoveries (%)	RSD (%/n = 7)	LOD (ng/L)	Compounds	Spiked (µg/L)	Recoveries (%)	RSD (%/n = 7)	LOD (ng/L)
Naphthalene	50	113.1	9.1	1.09	<i>p,p'</i> -DDE	50	83.7	9.7	0.65
Acenaphthene	50	92.3	9.2	1.06	Dieldrin	50	101.7	8.7	0.35
Acenaphthylene	50	95.2	8.4	0.51	Aroclor1260-1	100	91.6	8.6	1.05
Fluorene	50	86.9	7.4	0.95	Endrin	50	110.2	9.3	0.54
α-BHC	50	96.7	8.9	0.31	β-Endosulfan	50	102.1	9.9	0.65
β-BHC	50	97.1	8.7	1.09	<i>p,p'</i> -DDD	50	103.4	9.7	0.35
Hexachlorobenzene	50	87.3	9.7	0.80	Aroclor1260-2	100	90.9	8.7	1.08
γ-BHC	50	91.8	8.9	0.70	Endosulfan-sulfate	50	94.6	7.4	0.64
Phenanthrene	50	112.7	9.8	1.01	Endrin aldehyde	50	89.7	9.8	0.35
Aroclor1016-1	100	89.7	8.7	1.08	<i>p,p'</i> -DDT	50	91.2	9.5	0.50
Anthracene	50	94.6	9.8	0.70	Aroclor1260-3	100	92.4	8.7	1.07
δ-BHC	50	93.1	7.5	0.45	Benzo(a)anthracene	50	91.7	8.9	0.48
Aroclor1016-2	100	87.4	8.9	1.07	Chrysene	50	93.8	9.7	0.56
Heptachlor	50	103.2	8.9	0.80	Methoxychlor	50	89.6	9.4	0.46
Aroclor1016-3	100	85.8	9.1	1.07	Aroclor1260-4	100	90.5	8.7	1.03
Aroclor1016-4	100	87.9	8.7	1.05	Benzo[b]fluorathene	50	94.6	7.9	0.48
Aldrin	50	94.3	9.2	0.45	Benzo[k]fluorathene	50	87.6	7.9	0.50
Heptachlor epoxide	50	92.7	8.9	0.40	Benzo (a) pyrene	50	93.6	8.7	0.52
Fluoranthene	50	102.1	9.3	0.20	Indeno(1,2,3-cd)pyrene	50	93.3	9.9	0.57
Pyrene	50	105.9	9.7	0.65	Dibenz(a,h)anthracene	50	101.2	7.3	0.47
α-Endosulfan	50	110.4	9.9	0.55	Benzo(g,h,i)perylene	50	101.5	8.4	0.50

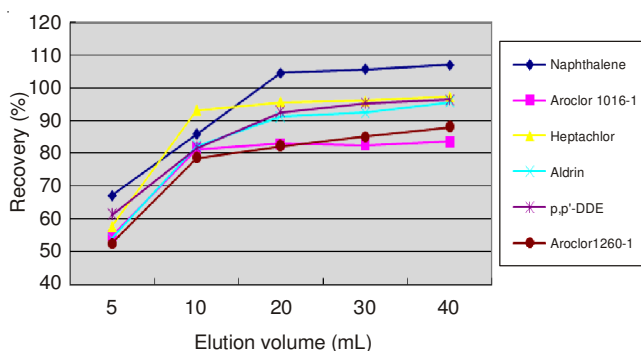


Fig. 3. *n*-Hexane elution curve

n-hexane as elution solvent, polychlorinated biphenyls and a part of organochlorine pesticides such as heptachlor, aldrin, *p,p'*-DDE etc., can be completely or mostly recovered and only naphthalene in polycyclic aromatic hydrocarbons can be mostly recycled. And then used *n*-hexane/dichloromethane (1:1) as elution solvent, drew the elution curve according to the above way, it turned out that used 20 mL *n*-hexane/dichloromethane (1:1) can recover residual organochlorine pesticides and polycyclic aromatic hydrocarbons. The method determined to use 20 mL *n*-hexane and 20 mL *n*-hexane/dichloro-methane (1:1) as elution solvent.

Recovery, RSD and LODs: Took 7 groundwater samples, added 50 µL standard, test all technological process according to experiment method, detect the precision and accuracy with results shown on Table-1. Under experiment conditions, results showed that recoveries of each target could reach 70-130 % with standard deviation below 10 % and detection limit could reach 0.2-1.1 ng/L, which could satisfy the daily water analysis requirement.

Actual sample analysis: We adopted this method to analyze water in river nearby industrial park and pharmaceutical factory. The results showed that 16 polycyclic aromatic hydrocarbons of different degrees were detected, with respective content of 20.3-994, 15.7-872 µg/L and organochlorine pesticides and polychlorinated biphenyls were detected with less quantity, only *p,p'*-DDE and *p,p'*-DDD were detected with the content of 6.75-10.01 and 3.47-7.21 µg/L, the content of polychlorinated biphenyls were 15.97 and 10.63 µg/L. Experiment results indicated that the river close to this two areas were polluted and attentions should be paid.

REFERENCES

- A. Aguilar and A. Borrell, in eds.: M.C. Fossi and C. Leonzio, Assessment of Organochlorine Pollutants in Cetaceans by Averages of Skin and Hypodermic Biopsies, In: Non-Destructive Biomarkers in Vertebrates, Boca Raton, FL. Lewis Publishers, pp. 245-268 (1994).
- K. Haraguchi, T. Endo, M. Sakata, Y. Masuda and M. Simmonds, *Shokuhin Eiseigaku Zasshi*, **41**, 287 (2000).
- D. Viale, *Int. J. Environ.*, **45**, 183 (1994).
- X.L. He, T.T. Xu, Y.Y. Zhang, J.T. Wang and N. Xia, *Rock Miner. Anal.*, **6**, 57 (2012).
- W.W. Dong, Y.J. Hao, D. Wang and Y. Xu, *Hubei Agric. Sci. Sci.*, **8**, 1693 (2011).
- T.F. Bidleman, M.D. Walla, R. Roura, E. Carr and S. Schmidt, *Mar. Pollut. Bull.*, **26**, 258 (1993).
- B.G. Loganathan and K. Kannan, *Ambio*, **3**, 187 (1994).
- S. Tanabe, H. Hidaka and R. Tatsukawa, *Chemosphere*, **12**, 277 (1983).
- Y. Wang, X.X. Zhi and L.J. Zhang, *J. Instr. Anal.*, **5**, 493 (2008).
- J. Fang and K.X. Wang, *Chin. J. Anal. Chem.*, **11**, 1607 (2007).
- Z.W. Xie, P. Yang, Ch. Liao, Ch.H. Ren, Ch.H. Guo, X.Q. Wu and J. Liao, *Environ. Moint. China*, **5**, 20 (2008).
- Environmental Protection Agency (EPA), Standard Methods for the Determination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Washington DC (1996).