

Determination of Organochlorine Pesticides in Coastal Waters of Qingdao City, China: a Comparison of GC-MS and GC-ECD Methods in Seawater Applications

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Introduction

Organochlorine pesticides (OCPs) are ubiquitous environmental organic micro-pollutants¹. The increasing risk to human health generated by the widespread use of OCPs in our environment is well established^{2, 3}. Although their production, usage and disposal have been regulated or prohibited in most of the developed countries since the 1970s, the use of OCPs remains widespread at present in many developing countries, especially in Asia, South America and Africa. In recent decades, many research studies have demonstrated that these contaminants could be transported through atmospheric deposition over long distances. In coastal waters in the proximity of a city such as QingDao with mixed commercial, industrial and agriculture activities, surface waters, runoffs and wastewaters constitute the major input of OCPs.

The determination of OCPs in different environmental matrices remains to be a challenging analytical task despite the extensive research effort devoted to the area in the past. In surface waters such as river or near-shore seawaters, interference is the major analytical problem because of the presence of humus, biologically derived substances, suspended particulate matters, etc, in addition to high concentration of pollutants.

The aim of this paper is to develop an effective method for the determination of OCPs in coastal water samples around QingDao City, which receives municipal sewers, runoffs from agricultural farmland, industrial wastewaters with potential OCP contaminations. Analytical methods consist of liquid-liquid extraction, florisil column clean up followed by GC analysis with μ ECD or MS detections have been developed and compared. Detection sensitivity, reproducibility and peak confirmation are the key issues in method development and they are individually addressed in the study. The developed methods have been applied to the determination of OCPs in real water samples as a part of a long term monitoring program undertaken in our laboratory.

Materials and Methods

All chemicals and sorbents were of analytical grade or better. A total of 6 near shore seawater samples were collected near QingDao city in China, as shown in Fig.1. 250 mL of water samples were extracted twice with 50 mL *n*-hexane each time. The extracts were combined and filtered through membrane (polycarbonate) filter (45 μ m). The filtrate was concentrated by rotary evaporation at 50 °C to a volume of about 1 mL. The concentrate was then transferred directly to an activated florisil column, and the OCP fractions were eluted with a mixture of diethyl ether/*n*-hexane (5:95) at a flow rate of 5 mL/min. Finally, the eluent was concentrated again by rotary evaporation and the final volume of the concentrate was made up to 1.0 mL volume for GC analysis. Two Agilent 6890N gas chromatographic systems were used for GC analyses. One is equipped with a ⁶³Ni Micro Electron Capture Detector (*m*ECD) and the other with an Agilent 5973N mass spectrometer detector. The two capillary columns used were HP 5 (30 m \times 0.32mm i.d., 0.25 μ m film thickness) and HP-5 MS (30 m \times 0.25mm i.d., 0.25 μ m film thickness).

Results and Discussion

Method Development

The GC separation was optimized by running the 15 pesticides standard solution spiked with internal standard using GC-MS. Heptachlor epoxide was chosen as the internal standards. A typical total ion chromatogram from GC/MS analysis is shown in Fig 2. The detection limits from Total Ion Monitoring (TIM) and Selected Ion Monitoring (SIM) modes were compared. In TIM, total MS response for each GC peak was obtained by full scan acquisition mode, but only the base peak in the MS spectra was used for quantitation. In SIM analysis, only the base peak of each

pesticide was monitored during MS detection. Least square fitted linear calibration lines were observed in the range of 0.1-100 mg/L for OCPs, with the correlation coefficients fall between 0.9807 and 0.9963. These results are listed in Table 1. The detection limits were 0.04-0.72 µg/L by SIM detection and 0.10-4.99 µg/L by TIM detection. From the results shown in Table 1 it can be observed that GC- μ ECD offers the highest sensitivity among the three detection modes, i.e., about 50-150 times higher than those of GC/MS by SIM, and up to 100 times higher than those of GC/MS by TIM.



Fig. 1. Location of sampling stations

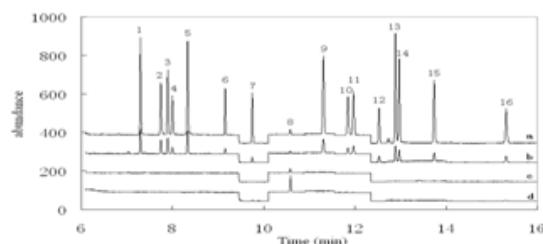


Fig. 2. Ion Chromatograms obtained by GC/MS under SIM acquisition mode of (a) standard solution (b) coastal water sample spiked with all standards (c) coastal water spiked with internal standard and (d) MILIQ water spiked with internal standard. Peak assignment: (1) α -HCH (2) β -HCH (3) γ -HCH (4) pentachloronitrobenzene (5) δ -HCH (6) heptachlor (7) aldrin (8) heptachlor epoxide (internal standard) (9) endosulfan (10) *p,p*-DDE (11) dieldrin (12) endrin (13) *p,p*-DDD (14) *o,p*-DDT (15) *p,p*-DDT (16) methoxychlor

Peak Confirmation in GC-ECD analysis

GC-ECD is among the most sensitive technique for chlorinated organics, and is one of the most frequently used methods in routine analysis for OCPs. The major problem of the method is peak identification and this is generally accomplished by the following methods:

1. Use multiple columns with different polarities to provide independent check of peak retention times. There are several kinds of columns that can be used for OCPs separation. The most often used are HP-5 or other similar nonpolar solid phases, and HP-1701 or similar intermediate polarity phases. Confirmation is established by the appearance of the suspected pesticides at the same retention times as the standards on different columns.
2. Use MS identification. The method, however, is often not sensitive enough in detecting trace OCPs in real environment samples, and thus appropriate trace enrichment technique during the sampling or analytical steps is needed. The method developed in this study has push down the detection limits for OCPs to 0.10~4.99 mg/L (see Table 1), which is marginally adequate for analyzing water samples for regulatory purposes (Chinese marine water quality regulation specifies that in seawater, the sum of OCPs cannot exceed 1 mg/L).
3. Use of characteristic chemical reactions. Some characteristic chemical reactions can be applied to confirm the existence of a certain OCP compound. For example, methanolic sodium can react and degrade δ -BHC and γ -BHC rapidly⁵. Thus, the running of samples with or without prior methanolic sodium treatment provides peak confirmation for the two compounds. This is illustrated in Fig. 3. A similar technique involves the treatment of samples by potassium dichromate-vitriol solution. The compounds can react and degrade *p,p*-DDE, resulting in the disappearance of the suspect peak along with the appearance of a peak corresponding to its degradation product *p,p*-dichlorodibenzophenone⁵. Standard (contain *p,p*-DDE) chromatography before and after the reaction with potassium dichromate-vitriol is shown in Fig. 4.

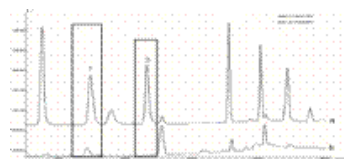


Fig.3 Standard chromatography before and after the reaction with sodium methanol (GC- μ ECD)

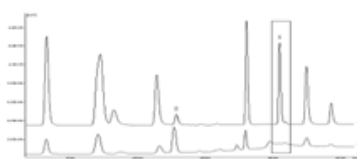


Fig.4 Standard chromatography before and after the reaction with potassium dichromate-vitriol solution (GC- μ ECD)

a before reaction b after reaction

1. γ -HCH 2. δ -HCH

a before reaction b after reaction

1. *p,p'*-DDE 2. *p,p'*-dichlordibenzophenone

Analysis of Seawater samples

The performance of the method for real samples was tested for MILIQ water (blank) and coastal water samples. First, a blank of MILIQ water was analyzed and the result showed the absence of contaminant peaks in the procedural blank. Then, 6 QingDao coastal water samples were analyzed and none of the target analytes were detected in these samples (Table 2). These samples were therefore used for recovery and precision studies. The reproducibility of the method was determined by performing three separate runs of the same seawater sample spiked with pesticide standards to concentrations ranged from 4-50 μ g/L. The relative standard deviation (R.S.D.) of GC/MS analysis ranged from 9.2 -21.8 % under SIM acquisition, as shown by the data listed in Table 1. The precision of this method was deemed acceptable for the analysis of environmental pesticides of concern.

Table 1 Comparison of linear dynamic range, correlation coefficients, recovery and limits of detection obtained for coastal water by three methods: (1) MS using SIM acquisition modes, (2) MS using full scan modes and (3) with μ ECD detection (see remarks in text)

Compound	MS (SIM)					MS (Scan)	μ ECD
	r^2	Linearity range (mg/L)	Recovery (%)	R.S.D. (%)	LOD ^a (mg/L)	LOD (mg/L)	LOD (mg/L)
α -HCH	0.9949	0.2-8.0	103.1	12.8	0.04	0.16	0.001
β -HCH	0.9950	0.2-8.0	111.9	9.4	0.14	0.21	0.001
γ -HCH	0.9941	0.2-8.0	107.7	9.9	0.06	0.14	0.001
pentachloronitrobenzene	0.9963	0.8-32.0	77.3	15.7	0.42	0.95	0.003
δ -HCH	0.9911	0.4-16.0	105.3	13.5	0.09	0.72	0.001
heptachlor	0.9920	2.0-8.0	62.3	17.1	0.05	0.16	0.001
aldrin	0.9954	0.3-11.2	61.8	21.8	0.09	0.06	0.001
heptachlor epoxide (i.s.)	nq ^b	nq	nq	nq	0.10	0.32	0.001
endosulfan	0.9932	2.8-100	92.0	14.8	0.72	4.99	0.018
<i>p,p'</i> -DDE	0.9954	0.1-4.8	82.0	16.7	0.08	0.50	0.001
dieldrin	0.9904	0.7-25.4	94.0	19.3	0.17	0.11	0.004
endrin	0.9937	0.8-30.4	86.8	12.2	0.59	0.64	0.004
<i>p,p'</i> -DDD	0.9929	0.2-8.0	83.7	9.2	0.07	0.37	0.001
<i>o,p'</i> -DDT	0.9954	0.2-8.0	76.1	11.3	0.04	0.80	0.001
<i>p,p'</i> -DDT	0.9938	0.2-8.0	78.7	12.5	0.09	1.00	0.001
methoxychlor	0.9807	0.3-11.2	90.0	18.2	0.24	0.70	0.002

a: Limit of Detection: Calculated by 3 times of signal to noise ratio

b: not qualified

Table 2 Analysis of OCPs in coastal water samples collected in Qingdao City

Sample	α -HCH	β -HCH	γ -HCH	pentachloro -nitrobenzene	δ -HCH	hepta- -chlor	aldrin	endo- p,p - sulfanDDE	dieldrin	endrin	p,p - DDDDT	o,p - DDT	p,p - methoxy -chlor
1	nd*	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

*: nd=not detected; limits of detection for each of the listed pesticides are given in Table 1.

Acknowledgements

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