Determination of chlordane in air by gas chromatography–mass spectrometry with selected ion monitoring

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ABSTRACT

A gas chromatographic–mass spectrometric (GC–MS) method for the determination of chlordane in air was developed. Chlordane collected in a Tenax-TA tube was thermally desorbed into a fused-silica capillary column and determined by GC–MS with selected ion monitoring. The relative standard deviation of the peak area obtained in recovery tests ranged from 1.1 to 5.1% and the limit of detection was 5 pg (signal-to-noise ratio = 4). This method was applied to determine chlordane in indoor and ambient air samples in Kitakyushu, Japan.

INTRODUCTION

Chlordane was first prepared in the 1940s by the condensation of hexachlorocyclopentadiene with cyclopentadiene to produce chlordene, which was then chlorinated to give chlordane. Technical chlordane includes more than ten isomers and by-products, the main components being *trans*-chlordane (24%), chlordene isomers (21.5%), *cis*-chlordane (19%), heptachlor (10%) and nonachlor (7%). Chlordane had been used as an insecticide to control termites. As it is a carcinogenic substance with low degradability and high accumulation in the environment [1,2], it was specified as designated chemical substance in 1986 and its usage has been regulated since 1987 in Japan.

According to the results of a GC–MS moni-

toring survey performed by the Environmental Agency of Japan [3,4], chlordane was detected in sea-bottom sediment, fish and shellfish. Further, there are some reports concerning chlordane in room air and ambient air [5–14]. Suzuki *et al.* [13] measured the concentration of chlordane in atmospheric air in Kanagawa Prefecture of Japan and in the indoor air of houses that had been treated with chlordane to control termites. Even 8–9 years after the treatment, the average indoor concentration of chlordane was more than 0.4 $\mu g/m^3$. They concluded that those who spent more than 18 h per day in such houses might have inhaled more than 0.5 $\mu g/kg$ (the acceptable daily intake mass/kg specified by the FAO/WHO). This result suggests that it is necessary to carry out long-term indoor monitoring in houses treated with chlordane.

Reported methods for determining chlordane in air include the following. Chlordane in air trapped by a solid adsorbent such as silica gel or

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porous polymer beads was extracted with an organic solvent and determined by GC on a packed column with electron-capture detection. This method gave low chromatographic separation. Suzuki [15] developed a multi-dimensional GC method with MS with selected ion monitoring (GC–MS-SIM). In this method, chlordane trapped in a tube containing GC packing material (OV-17) was thermally desorbed and determined by GC–MS-SIM. However, this system is complicated and difficult to handle. Moreover, the analytical column might be polluted by bleeding of the packing material in the collection tube.

In this paper, we report a simple method for chlordane determination in which Tenax-TA is used as the trapping material and capillary GC–MS-SIM is used for analysis.

EXPERIMENTAL

Reagents

Heptachlor, oxychlorden, cis-nonachlor, trans-nonachlor, cis-chlordane and trans-chlordane were purchased from Wako. A mixed standard solution (2 ng/μl of each) was prepared in hexane.

Apparatus

Fig. 1 shows the sampling tube used in this experiment. A glass-lined stainless-steel tube (150 mm × 8 mm O.D. × 4 mm I.D.) (GL Science) was packed with 0.4 g of Tenax-TA (20–40 mesh) (GL Science) and both ends of the tube were sealed with silica-wool and connected with reducing unions (8 mm/3 mm). Before use, purified nitrogen was passed through the tube at 280°C overnight for cleaning. Air samples were collected at a flow-rate of 1 l/min by a diaphragm pump (Shibata Kagaku) equipped a
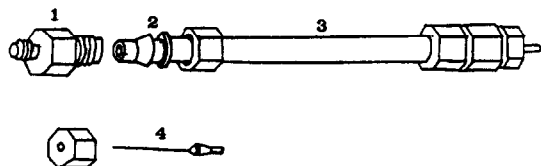

Fig. 1. Tenax-TA tube. 1 = Reducing anion; 2 = ferrule; 3 = glass lined stainless-steel tube; 4 = needle.

needle valve to control the flow-rate. A 3 mm O.D. stainless-steel bar was used as a stopper. After sampling, the sampling tube was stored in a refrigerator until analysis. This tube was reused after the above-mentioned cleaning.

A thermal furnace which raises the temperature from 50 to 300°C in 2 min was purchased from the Tanaka Rikagaku Kikai.

The GC–MS system consisted of a Hewlett-Packard HP 5890J gas chromatograph and a JEOL JMS-DX 303 mass spectrometer with a DA-5000 data system.

Thermal desorption system and procedure

The thermal desorption system connected with the GC–MS system is shown in Fig. 2. A three-way tap (3) was connected with the outlet of the mass flow controller of the gas chromatograph. Another three-way tap (4) was connected to this line. Two stop valves were connected to the split and splitless vent of the gas chromatograph.

By closing these stop valves, the total flow-rate of carrier gas, most of which is usually vented to waste, passed through to the analytical column. As a result, the total flow-rate of the carrier gas
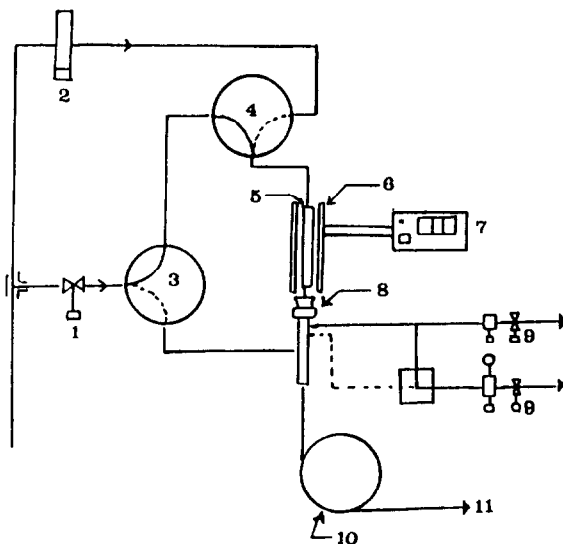

Fig. 2. Thermal desorption diagram for GC–MS analysis for chlordane. 1 = Mass flow controller valve; 2 = flow controller; 3 = three-way tap (A); 4 = three-way tap (B); 5 = Tenax-TA tube; 6 = electric furnace; 7 = control unit; 8 = injection port; 9 = stop valve; 10 = capillary column; 12 = ion source.

was 40 ml/min and the head pressure was up to ca. 500 kPa.

The analytical procedures were as follows. (a) After the Tenax-TA tube had been purged for 2 min by turning tap (3), it was connected to the injection port of the gas chromatograph. (b) After taps (3) and (4) had been turned, the Tenax-TA tube was heated at 300°C for 20 min by the furnace; during desorption, the GC column temperature was maintained at 50°C. (c) The two stop valves were opened and the trapped substance was measured by GC–MS. A direct coupling method is usually used for interfacing a capillary column to the MS ion source. However, it was difficult in our experiment to maintain a vacuum of the ion source, because the flow-rate of carrier gas (40 ml/min) was very high during desorption. Therefore, a capillary column was connected to the MS ion source through the quartz glass jet separator which is used to connect the GC and MS systems. The flow-rate of the make-up gas was 30 ml/min.

GC–MS-SIM procedure

The GC–MS conditions are given in Table I. The resolution of the mass spectrometer in the SIM mode was about 500 and the switching rate was 0.1 s per ion. To obtain the accuracy of the peak area, m/z values in the SIM mode were set at 271.810 and 273.810 for heptachlor, 387.800 for oxychlordane, 370.828 and 372.828 for cis, trans-chlordane and 407.790 and 408.790 for cis, trans-nonachlor.

RESULTS AND DISCUSSION

Recovery tests of standard mixtures were carried out as follows. Three glass-lined stainless-steel tubes were connected in series. The first and third were Tenax-TA tubes and the second was packed with silica-wool. After 2 μl of standard solution containing 4 ng of each standard had been added to the second tube, the tube was heated to 100°C in the furnace. Indoor air was passed through these three tubes at a flow-rate of 2 l/min until the total flow reached 50–100 l. Impurities in room air were removed in the first tube and vaporized standard in the second tube was trapped in the third tube. Then, two kinds of thermal desorption method were performed: one was the front desorption method (FD method) in which the standard was desorbed from the sampling tube inlet; the other was the back desorption method (BD method) in which the standard was desorbed from the sampling tube outlet.

Recovery test results obtained by the FD method are given in Table II. A typical SIM chromatogram of chlordane standard mixture obtained in the recovery test is shown in Fig. 3. Most of the relative standard deviations (R.S.D.s) were less than 5%. The reproducibility

TABLE I

GC–MS CONDITIONS FOR DETERMINATION OF CHLORDANE

Column	HP Ultra-2 (5% phenyl–95% methylsilicone) fused-silica capillary column, 25 m × 0.32 mm I.D., 0.52 μm film thickness
Temperatures:	
Column	Programmed: 1 min at 50°C, 30°C/min to 150°C, 10°C/min to 280°C, 6 min at 280°C
Injection	200°C
Inlet	250°C
Ion source	200°C
Carrier gas	Helium
Linear velocity	2 ml/min
Ionization method	Electron impact
Emission current	300 μA
Switching rate	0.1 S per ion

TABLE II

REPRODUCIBILITY OF PEAK AREA OBTAINED BY THE THERMAL DESORPTION METHOD (FD METHOD) ($n = 5$)

The amount added was 4 ng each.

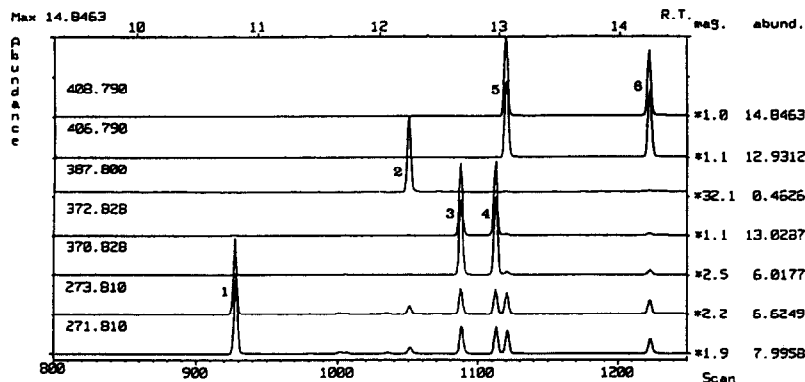| Compound	Peak area	R.S.D. (%)
Heptachlor	1.69	3.7
Oxychlordane	0.54	1.1
trans-Chlordane	2.17	5.1
cis-Chlordane	2.25	4.8
trans-Nonachlordane	2.70	4.0
cis-Nonachlordane	2.23	4.5

Fig. 3. SIM chromatogram of chlordane standard mixtures obtained by thermal desorption. 1 = Heptachlor; 2 = oxychlordane; 3 = trans-chlordane; 4 = cis-chlordane; 5 = trans-nonachlor; 6 = cis-nonachlor. R.T. = Retention time in min; mag. = magnification; abund. = abundance.

of the retention time of standards desorbed by the FD method is shown in Table III. The standard deviation was less than 2 s for each compound.

In our experiment, during desorption, carrier gas was passed through the capillary column at a flow-rate of 20–30 ml/min; however desorbed low-volatile components such as chlordane were retained in the inlet part of the capillary column without any cold trap. The detection limit of the method for each compound was 5 pg (signal-to-noise ratio = 4), which was estimated to represent 0.25 ng/m^3 on collecting 20 l of air.

Comparison of two kinds of desorption method

In this method, if there are no leakages in the system, all thermally desorbed substances can be

introduced into the analytical GC column. It was predicted that a peak area obtained with this method would be larger than the peak area with syringe injection (syringe injection of hexane solution containing a standard by the splitless method) in GC–MS, because sample discrimination occurs in the splitless injection of low-volatile compounds. Peak areas obtained from FD method, the BD method and syringe injection were compared. The results are given in Table IV for a comparison of each method when the peak area of the splitless method is taken as 100%. The FD method was the most effective for introducing samples into the GC–MS system, because the peak area was about three times larger than that in the splitless method. This means that sample discrimination did not occur in the FD method and, as a result, a lower limit of detection can be obtained.

In the BD method, the peak areas of all

TABLE III

REPRODUCIBILITY OF RETENTION TIME BY THERMAL DESORPTION METHOD ($n = 5$)

' = min; " = s.

Compound	Syringe injection	Thermal desorption
Heptachlor	13'36" ± 0.5"	13'41" ± 0.9"
Oxychlordane	15'12" ± 0.5"	15'16" ± 1.0"
trans-Chlordane	15'40" ± 0.7"	15'45" ± 0.8"
cis-Chlordane	15'59" ± 0.5"	16'4" ± 1.0"
trans-Nonachlordane	16'4" ± 0.6"	16'8" ± 1.0"
cis-Nonachlordane	17'22" ± 0.4"	17'27" ± 1.1"

TABLE IV

COMPARISON OF PEAK AREAS WITH THE THERMAL DESORPTION METHODS ($n = 5$)

Compound	BD method	FD method	BD/FD
Heptachlor	n.d.	2.5	–
Oxychlordane	1.7	2.4	0.71
trans-Chlordane	2.3	3.2	0.72
cis-Chlordane	2.3	3.1	0.74
trans-Nonachlordane	2.1	3.2	0.65
cis-Nonachlordane	2.1	3.2	0.67

compounds were relatively small and especially heptachlor was not desorbed from the Tenax-TA tube. This suggests that degradation of heptachlor was taking place in the Tenax-TA tube during desorption. In order to confirm the decomposed substance, after adding 100 ng of heptachlor the total ion chromatogram (TIC) of desorbed components from the Tenax-TA tube was obtained. However, no decomposed substances were found on the TIC. Reactions of halogenated compounds with Tenax during thermal desorption have been reported [16] and recoveries of bromotrichloromethane and pentachloroethane added to Tenax were conspicuously poor. Tri- and tetrachloroethane which were not added were desorbed from Tenax. In our experiment, although no decomposed substances were detected, there is a probability that other compounds except heptachlor are slightly decomposed in the Tenax-TA tube during desorption, because the recovery of other compounds is about 30% lower in the BD than in the FD method.

Measurement of desorption time and breakthrough volume

Desorption in the recovery test was carried out for 20 min. To determine the accurate desorption time of standard mixtures from the Tenax-TA tube at a desorption temperature 300°C, the FD and BD methods were applied. After the two stop valves had been closed and the GC column temperature was held at 280°C, the

elution times of standard mixtures were measured. A SIM chromatogram obtained by the BD method is shown in Fig. 4. The elution time of cis-nonachlor, which was the least volatile compound tested, was about 18 min. As the elution time is equal to the desorption time at the desorption temperature, 300°C in this experiment, it takes about 18 min to desorb all the tested compounds by the BD method. On the other hand, the elution time in the FD method is about 10 min. The FD method is superior to the BD method because the desorption time is very short and no degradation occurs.

To estimate the breakthrough volume of low-volatile compounds such as chlordane, an extrapolation method has been used [17]. This is a method for the determination of retention volumes at ambient temperature by linear extrapolation of retention volumes at higher temperature. The retention volume of desorbed compounds by the above-mentioned experiment (BD method) was considered as the retention volume of the adsorbent in the Tenax-TA tube. The breakthrough point is regarded as the start of the peak on the chromatogram. We attempted to estimate the breakthrough volume of trans-nonachlor at ambient temperature. The breakthrough volumes of trans-nonachlor at eight temperatures between 200 and 340°C were obtained. These values were compensated using the equation for the corrected specific retention volume.
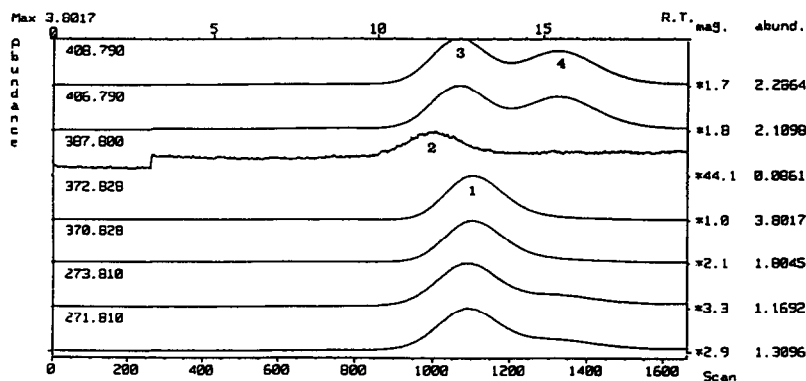
A linear regression equation, $\log V_r = -3.41 +$

Fig. 4. Elution peak of chlordane standard mixture obtained from Tenax-TA tube by thermal desorption. 1 = Oxychlordane; 2 = trans-chlordane + cis-chlordane; 3 = trans-nonachlor; 4 = cis-nonachlor.

$1.96(1/T)$ (where V_r is in m^3), was obtained from the relationship between $\log V_r$ and $1/T$. The breakthrough volume of *trans*-nonachlor from this equation at ambient temperature (25°C) was $1.5 \ m^3$ on the Tenax-TA tube. This value was sufficient for sampling indoor and ambient air, because the sampling volume was less than 100 l in our experiment.

Measurement of chlordane in indoor air and ambient air

The method was applied to indoor and ambient air samples. Analysis was carried out on several samples collected in the living rooms of houses that had been treated with technical chlordane and ambient air in Kitakyushu City. The volume collected was 20 l for indoor air and 100 l for ambient air for each sample. The SIM

chromatograms of house 2 indoor air and ambient air are shown in Fig. 5 and the concentrations are given in Table V. Five compounds (heptachlor, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and *cis*-nonachlor) were found in every sample except for oxychlordane, which was a metabolite. The peak patterns of both SIM chromatograms were similar to that of technical chlordane. For example, peaks 6 and 7 in Fig. 5, which are isomers in technical chlordane [18], were detected in every sample. The approximate composition of the five compounds in technical chlordane used in Japan is heptachlor 11–17%, *trans*-chlordane 32–40%, *cis*-chlordane 21–32%, *trans*-nonachlor 15–20% and *cis*-nonachlor 2–10%. The composition of the sample was similar to that of technical chlordane. The total concentration of the five compounds in house 1 that had
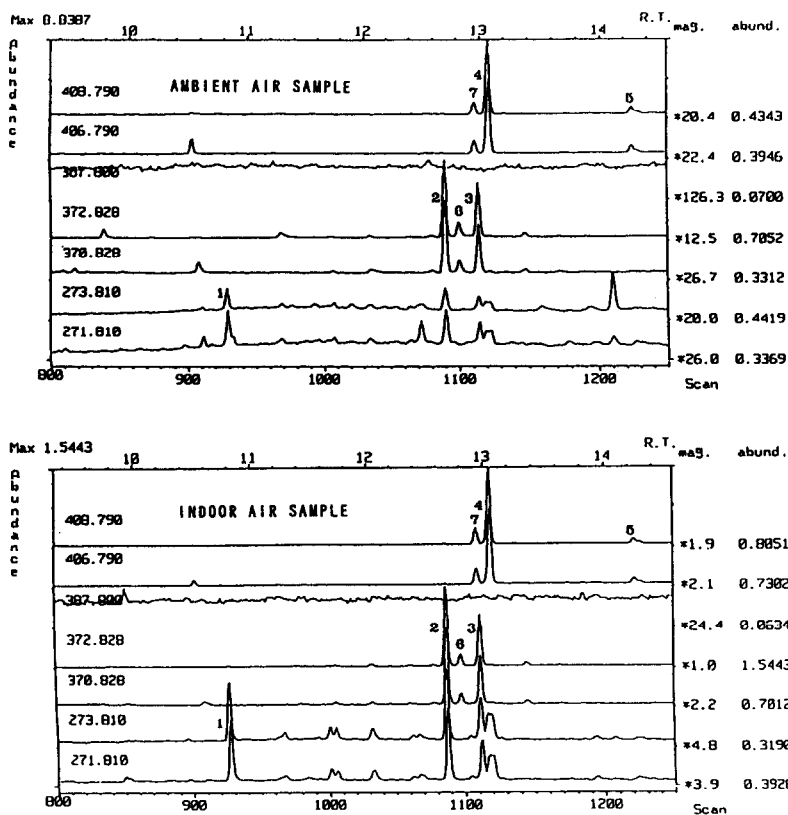

Fig. 5. SIM chromatogram of an indoor air sample (house 2) and ambient air sample in Kitakyushu City. The values following the asterisks are the magnification factors of the chromatograms. 1 = Heptachlor; 2 = *trans*-chlordane; 3 = *cis*-chlordane; 4 = *trans*-nonachlor; 5 = *cis*-nonachlor; 6, 7 = not identified.

TABLE V

CONCENTRATIONS OF CHLORDANE IN INDOOR AIR AND AMBIENT AIR IN KITAKYUSHU

Compound	Chlordane concentration (ng/m^3)		
	House 1[a]	House 2[a]	Ambient Air
Heptachlor	130	6.0	0.23
Oxychlordane	n.d.	n.d.	n.d.
trans-Chlordane	75	12.3	0.61
cis-Chlordane	61	7.6	0.45
trans-Nonachlordane	35	5.5	0.35
cis-Nonachlordane	30	0.46	0.053

[a] House 1 had been treated with technical chlordane 3 years previously and house 2 had been treated 5 years previously.

been treated with chlordane 3 years previously was more than 200 times higher than that in outdoor air.

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