CARBON AND CHLORINE ISOTOPE ANALYSIS FOR HEXACHLOROBENZENE

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Introduction

Hexachlorobenzene (HCB) is one of the listed persistent organic pollutants (POPs) under the Stockholm Convention. It is mostly released as a by-product from industrial facilities. Its half-life in the ambient air is about 80 days[1]. Due to its slow photochemical degradation, HCB tends to transport over a long distance[1-2]. In the ambient air, HCB travels via wet deposition such as rains and snows into soils and water, where its movement between media is promoted by re-volatilization or sedimentation[3-5]. It is not easy, however, to identify HCB sources accurately because various sources release HCB and in Korea, particularly, HCB possibly transports over a long range from China[6]. In recent years, a technique began to be used to trace pollution sources or identify the transport of pollutants by analyzing and determining subtle differences between isotopes of pollutants. Case studies have also been reported on the analysis of carbon and chlorine (Cl) isotopes for some POPs. Carbon isotopes of PAHs were studied by Mikolajczuk[7], Dameng[8] and Zhang[9]. Individual Cl isotopes of PCBs were investigated by Mandalakis[10]. No analysis study on carbon and Cl isotopes of HCB, however, has been reported yet. In this view, this study was purposed to analyze carbon and Cl isotopes of HCB and use these isotopic values to identify HCB sources. The carbon isotopes of HCB were analyzed with the EA-IRMS and GC-C-IRMS, while the Cl isotopes were measured with the GC-MC-ICP-MS.

Materials and methods

To analyze HCB isotopes, two powder standard references were purchased from Fluka (99.9%, SZBC066XV, USA) and prepared. For the EA-IRMS analysis, these two individual products were weighed with a precision balance (AT21, Mettler Toledo) to bring them to about 1.2 mg, which were then put into tin boats (4 mm×4 mm×11 mm) and sealed. For the GC-C-IRMS and GC-MC-ICP-MS analysis, the same balance was used to dissolve 20 mg of the same powder standard reference in 10 mL of hexane to make a standard solution. This solution was then diluted to make solutions of various concentrations. The instrumental settings of the elemental analyzer (EA, Vario Micro Cube, IsoPrime Ltd., UK) were as follows: adsorption was performed at 1,150 ℃ for the combustion tube; 850 ℃ for the reduction tube; and 45 ℃ for the adsorption column. Desorption was then conducted at 90 ℃. The HP 5MS (30 m × 0.25 mm × 0.25 μm) was used for the column of the gas chromatograph (GC, Agilent 7890, Agilent, USA). The inlet temperature was 280 ℃ and the column flow was 1 mL. The split ratio was 3:1. The injected amount of the sample was 1 μL. The sample was held in the oven at 100 ℃ for two minutes. Then the oven temperature was raised at 5 ℃/min to 200 ℃ and at 20 ℃/min to 280 ℃, at which the sample was held for five minutes. The instrumental parameters of the isotope ratio mass spectrometer (IR-MS, IsoPrime 100, IsoPrime Ltd., UK) are shown in Table 1.

Table 1. Instrumental parameters of IR-MS for C isotope measurement

Source Parameter	CO_2	N_2	CO	SO_2	H_2
Accelerating voltage(V)	3795.63	3959.29	3952.95	2440.87	4317.58
Extraction voltage	72	75.98	68.40	66.23	82.54
Half plate differential(V)	- 96.57	- 95.78	- 86.22	- 72	- 76.37
Z plate voltage(V)	- 69.94	- 82.95	- 59.03	- 41.65	- 16.09
Electron volts(eV)	73.89	69.92	67.43	71.76	100
Ion repeller voltage(V)	- 5	- 4	- 7	- 5	42
Trap current(μA)	200	200	200	200	600
Magnet current(mA)	4000	3000	3000	3800	890

As the parameters of GC (Agilent 7980A, Agilent, USA) for the GC coupled MC-ICP-MS, the Restek MXT-1 (0.53 mm × 30 m) was used as the column, and 5 μL of the sample was injected. The inlet temperature was 300℃. The column flow was 30mL. The makeup gas was operated at 300 mL/min in the splitless mode. The temperature of the oven was kept at 100 ℃ for two minutes and then raised at 50 ℃/min to 250 ℃, at which the sample was held in the oven for ten minutes. Again, the temperature was raised at 50 ℃/min to 300 ℃, where the sample was held for five minutes. To prevent HCB separated by the GC from being condensed or adsorbed to the linkage between GC and MC-ICP/MS, heating coils were used to keep the temperature of the linkage at 170 ℃ during the analysis. The Cl stable isotope ratios of HCB were analyzed using the MC-ICP/MS (NP II, Nu, U.K.). Unlike general MC-ICP/MS analyses, the GC-MC-ICP/MS analysis injects samples into the MC-ICP/MS via carrier gas. Accordingly, the pressure of nebulizer gas was adjusted to 2.0 psi, and Ar mix gas was additionally used at 1 mL/min. To avoid interference effects by $^{1}H^{36}Ar$ on ^{37}Cl, the pseudo high resolution mode ($m/\Delta m$ = ~ 8000) was applied during the analysis, which resulted in ^{37}Cl peak plateau at 0.005 amu. The instrumental analytical sensitivity was optimized using 1000 ppm NH_4Cl reagent. The total signal of the Faraday detector was about 1 V.

Table 2. Instrumental parameters of MC-ICP/MS for Cl isotope measurement

Parameters	Values	Parameters	Values
MC-ICP/MS instrument	Nu Plasma II	Mix gas (Ar)	1 L/min
RF power	1300 W	Pump speed	18 rpm
Analyzer pressure	6.0 x 10^{-9}mbar	Cone	Ni
Coolant gas flow	13.0 L/min	Analyzer pressure	6.0 x 10^{-9}mbar
Auxiliary gas flow	0.8 L/min	Mass resolving power	~ 8000
Nebulizer type	GE micromist	Detector	Faraday detector
Nebulizer pressure	2.0 psi		(H6 for ^{37}Cl, L4 for ^{35}Cl)

Results and discussion

(1) Analysis of carbon isotope ratios

As the carbon isotopic composition, the delta value (δ) was expressed in per mill (‰) after the reference standard's $^{13}C/^{12}C$ isotope ratios ($R_{standard}$) and the sample's carbon isotope ratios (R_{sample}) were calculated in parts per thousand. The isotope ratios of the samples were corrected using the isotope ratios of CO_2 reference gas, a working standard. This CO_2 reference gas was corrected by the USGS 24 standard which was corrected based on the international reference material Pee Dee Belemnite (PDB) and provided by the International Atomic Energy Agency (IAEA). Using the EA-IRMS, carbon isotope ratios were analyzed for two HCB standard references (HF1 and HF2) in the powder form (Fluka, 99.9%). The injected HCB sample was about 300 μgC (HCB 1.2 mg), the minimum injected amount of carbon, of which accuracy was verified in a previous study[11]. The carbon isotope ratio of HF1 was -26.07 ‰ (± 0.063 ‰) and the precision was 0.24%. The carbon isotope ratio of HF2 was -26.03 ‰ (± 0.008 ‰) and the precision was 0.03%. Their mean value was -26.05 ‰. The difference between HF1 and HF2 ratios was 0.16%.

Table 3. Delta values of carbon isotopes for HCB using EA-IRMS

Sample	$\delta^{13}C$	N. of Sample	Stdev (%)	Relative stdev (%)
HF1	-26.07	5	0.063	0.24
HF2	-26.03	3	0.008	0.03
Mean value	-26.05			

For HF1, which showed -26.07 ‰ as its carbon isotope ratio, a standard solution was made for the GC-C-IRMS analysis. After the detection time of HCB was checked with the FID in the same GC, injection into the IRMS was performed. The time for IRMS detection was 1258.1 seconds on average. As shown in Table 4, the carbon isotope ratios were checked for HCB concentrations of 50 μg/mL to 5,000 μg/mL. When the concentration was 5,000 μg/mL, the carbon isotope ratio was -25.87‰ (± 0.1 ‰). The precision became higher along with the increase in HCB concentration: the precision was 1% or less at concentrations of 2,000 μg/mL or higher.

Differences from the EA analysis were reduced as the concentration increased: 1 % or less at concentrations of 5,000 μg/mL or higher. Unlike the EA analysis, where the total volume of the sample is injected into the IR-MS, only 1 μL of the sample is injected for the GC-C-IRMS. Because some amount of the sample is lost in the process of splitting during the GC analysis, the volume actually injected into the IR-MS is very little compared with that for the EA analysis. As a result of analyzing the standards, the concentration should be 5,000 μg/mL or higher to obtain significant values. In this view, the concentrating process and the increase in the injected sample volume should be further studied to analyze the trace carbon isotopes of HCB in environmental or emission gas samples.

Table 4. Delta value of carbon isotope for HCB using GC-C-IRMS(n=5).

Conc. (μg/mL)	Carbon conc. (μgC/mL)	$\delta^{13}C$ (GC-IRMS) (‰)	STDEV (‰)	RSD (%)	$\delta^{13}C$ (EA-IRMS) (‰)	Percent difference (EA-GC) (%)
50	13	-25.97	8.22	31.7	-26.07	0.4
75	19	-22.46	2.61	11.6	-26.07	14.9
100	25	-24.56	2.61	10.6	-26.07	6.0
250	63	-24.75	1.38	5.6	-26.07	5.2
500	126	-24.49	1.05	4.3	-26.07	6.2
1000	253	-24.96	0.59	2.4	-26.07	4.4
2000	506	-25.32	0.20	0.8	-26.07	2.9
3000	758	-25.53	0.25	1.0	-26.07	2.1
4000	1011	-25.73	0.06	0.2	-26.07	1.3
5000	1264	-25.87	0.10	0.4	-26.07	0.8

Since there are no previous studies focused on HCB isotopes, it is hard to make a direct comparison. Some studies have reported on carbon isotopes of similar POPs and other substances that are predicted to be HCB precursors. The analysis by Mikolajczuk[7] showed that carbon isotope ratios of PAHs in urban and rural dust ranged between -36.2 ‰ and -24.8 ‰. Zhang[9] carried out a comparative study on carbon isotope ratios of PAHs in particulate matters of cooking fumes (CF) and environmental tobacco smoke (ETS) and found that the isotope ratios ranged from -29.32 to -21.76 ‰. According to Dameng[8], carbon isotope ratios of PHAs from coal burning and coking plants were in the range of -28.8 ‰ to 24.0 ‰. Similar with dioxin, HCB is known to be formed from chlorination in de novo synthesis of precursors such as benzene[12]. Given that benzene is one of HCB precursors, HCB isotope ratios can be compared with benzene isotope ratios. According to Turner[13], the TD-GC-IRMS analysis showed that the carbon isotope ratio of benzene from stacks was 23.5 ‰ (± 0.11 ‰) and the ratio of benzene from vehicles was -24.5 ‰ (± 0.17 ‰). Similarly, Eckstaedt[14] found that benzene from calciners and stacks had a carbon isotope ratio of -23.2 ‰ (± 1.5 ‰). According to Eckstaedt[15], the carbon isotope ratio of benzene from vehicle exhaust gases was -21.7‰ (± 0.2 ‰). The range of these PAHs and benzene carbon isotope ratios were so wide that this study's HCB carbon isotope ratios fell within the range, but these findings seem to be insufficient to make a direct comparison with the carbon isotope ratios of HCB analyzed in this study.

(2) Analysis of Cl isotope ratios

Generally, Cl isotope ratios are shown as deviations from the isotope ratios of reference seawater chloride[16]. This study, however, presented the Cl isotope ratios of the analytic samples as absolute values because no isotope ratios have been reported from the GC-MC-ICP/MS system. In this study, the $^{37}Cl/^{35}Cl$ isotope ratio of 100 μg/mL HCB sample was 0.3445 (± 0.0030, 2SD) (Table 3, Figure 1). Since no data on $^{37}Cl/^{35}Cl$ isotope ratios of HCB samples could be found in previous studies, it was impossible to make a direct comparison of accuracy. However, Berglund and Wieser[17] reported that the isotope ratio of Cl in nature is 0.3200. According to Van Acker[18], Cl isotope ratios were measured for 24~165 μg Cl of TCE (trichloroethene) and PCE (tetrachloroethene), and the deviations (2σ) ranged between 0.0008 and 0.0025. Similar precisions were observed in this study by injecting 0.4 μg Cl, only 1/60 ~1/400 of the amount reported by Van Acker[18], which gives significance to this study. Considering that the concentrations of ambient organic pollutants including HCB are very low, it is assumed that the analysis of Cl isotope ratios using the GC-MC-ICP-MS in this study is likely to be a good method.

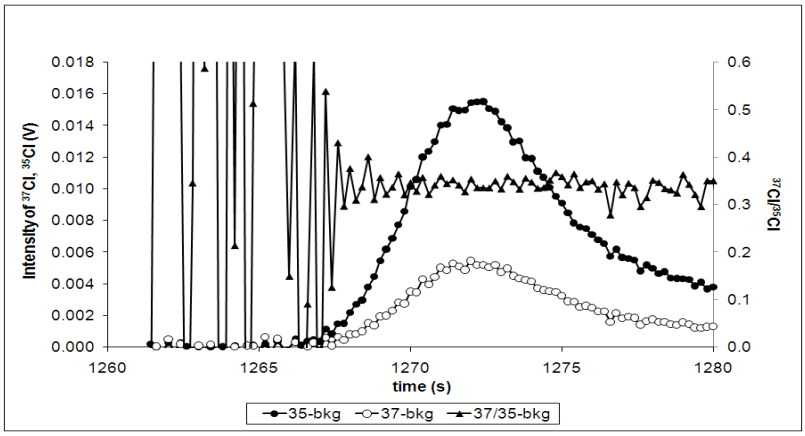

Figure 1. Chromatogram of 100 µg/mL hexachlorobenzene solutions obtained with GC coupled MC-ICP/MS (open circles, closed circles and closed triangles represent ^{35}Cl, ^{37}Cl, $^{37}Cl/^{35}Cl$ ratios, respectively).

(3) Conclusion

This study was conducted to promote the analysis of stable isotope ratios as a method of identifying HCB sources given that HCB is currently raising concerns because its long-range transport makes it hard to trace its sources. To this end, basic analysis of carbon and Cl isotope ratios of HCB was made. The result showed that the carbon isotope ratio was -26.07 ‰ (± 0.063 ‰) when measured with the EA-IRMS (1.2 mg injected), while it was -25.87‰ (± 0.1 ‰) when analyzed with the GC-C-IRMS at 5,000 ug/mL. As for Cl isotopes, the 37Cl/35Cl ratio was 0.3445 (±0.0030, 2SD) with the GC-MC-ICP-MS at 100 ug/mL. Although this study used standard references for the analysis because no previous research has reported on the analysis of carbon and Cl isotope ratios for HCB, its findings seem to be significant. Further studies need to be conducted to improve analysis techniques and characterize field samples.

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