GC AND GC-MS ANALYSIS OF POLYCHLORINATED DIOXINS, DIBENZOFURANS, AND AROMATIC HYDROCARBONS IN FLYASH FROM INCINERATORS AND FROM COAL-BURNING WORKS AND STEAM-ENGINES

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It has been reported by many researchers that flyash effluents from incinerators contain polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans(PCDFs) and polychlorinated aromatic hydrocarbons (PCAHs), which display widely varying toxicities.

A considerable volume of information about quantitative relationships between structures and toxicities has been accumulated on those compounmds in the last two dacades.

Recently, determination of polycyclic aromatic hydrocarbons and chlorinated ones in flyash samples from coal-burning burners of various gas works and from chimnies of coal-burning steam-engines of locomotives, was performed with gas chromatography(GC) and gas-chromatograph-mas-spectrometry(GC-MS)[1] and the toxicities of PAHs in petroleum pollutants were communicated.[2]

Isomer specific analysis of chlorinated dioxins and other compounds by GC and GC-MS using polymeric liquid crystal stationary phases was published[3] and a paper on mechanisms of formation of PCDDs and PCDFs in petroleum refining process was read at the Third International Symposium on Environmental Research Topics, in Phenix.[4]

This paper deals with results of a co-operative research work on analysis of isomers in PCDDs and PCDFs, and of homologues in PCAHs, of flyash samples from incinerators and coal-burners, with GC and GC-MS techniques, and deals with a shape selec-

tive aspect to chromatographic retention behaviors and to geometrical and positional structures of those isomers.[5]

Flyash samples were obtained from the Hiroshima and Machida incinerators in Japan, and from the coal-gas producing works and chimnies of the coal-burning steam-engine locomotives in China.

GC and GC-MS analyses were performed with a Shimadzu GC and Shimadzu-Krato GC-MS in Hiroshima, with a Hewlett-Packard HP-5880A GC-FID, HP-5887A EI-CI-MS, and HP-5890/5970 MSD GC-EISIM-MS in Waterloo, and with a Varian 3700 GC-FID and Finigan MAT 312 MS in Dalian.

The amounts of polychlorobenzenes(PCBs), polychlorophenols(PCPs), PCDDs and PCDFs contained in flyash samples from the Machida incinerators were determined to be that hexa-, hepta- and octa- chlorodibenzo-p-dioxins(H6CDDs, H7CDDs and OCDD respectively) and dibenzofurans(H6CDFs, H7CDFs, and OCDF respectively) presented in the all samples. However, the amounts of tetra- and penta- chlorinated isomers(T4CDDs, T5CDDs, T4CDFs, and T5CDFs) were in the very low levels of 0.1 to 9 ng/g of flyash in most of the Machida samples.

It should be brought notice to us that the levels of the relatively more toxic tetra- and penta- chlorinated isomers as well as other PCDD and PCDF isomers in all these samples are extremely low, contrary to those of the flyash samples from the Onatrio Incinerators.

The amounts of PCDDs and PCDFs contained in flyash samples from the Hiroshima incinerators were determined more or less in all samples, and T4CDD, T4CDF, T5CDD, T5CDF isomers were in not so low levels in most of the Hiroshima flyash samples. About 130 isomeric compounds of PCDDs and PCDFs from the Hiroshima and Machida incinerators were analyzed and compared to those found in the flyash samples from the Kyoto, Ontario, Paris and Oslo incinerators.

The garbage treatment prior to incineration in Machida is differnet from the Ontario incinators. Only the conbustible materials were incinerated in the Machida incinerators which are fluidized bed design with calcium-oxide injection into the bed. Mechanisms of formation of PCDDs and PCDFs are discussed from these results.

Many chlorinated aliphatic and aromatic hydrocarbons in the flyash of the coal-burning works in China were found in the all samples. About 130 PCAHs of the Dalian works were determined. The results of the flyash samples from the gas works showed that H7CDDs, H7CDFs, OCDD and OCDF presented in the very low levels, as shown in Table I.

However, tetra- to hexa- chlorinated isomers were either not observed or were in the negligibly detected levels. Isomer specific analyses of those flyash samples of

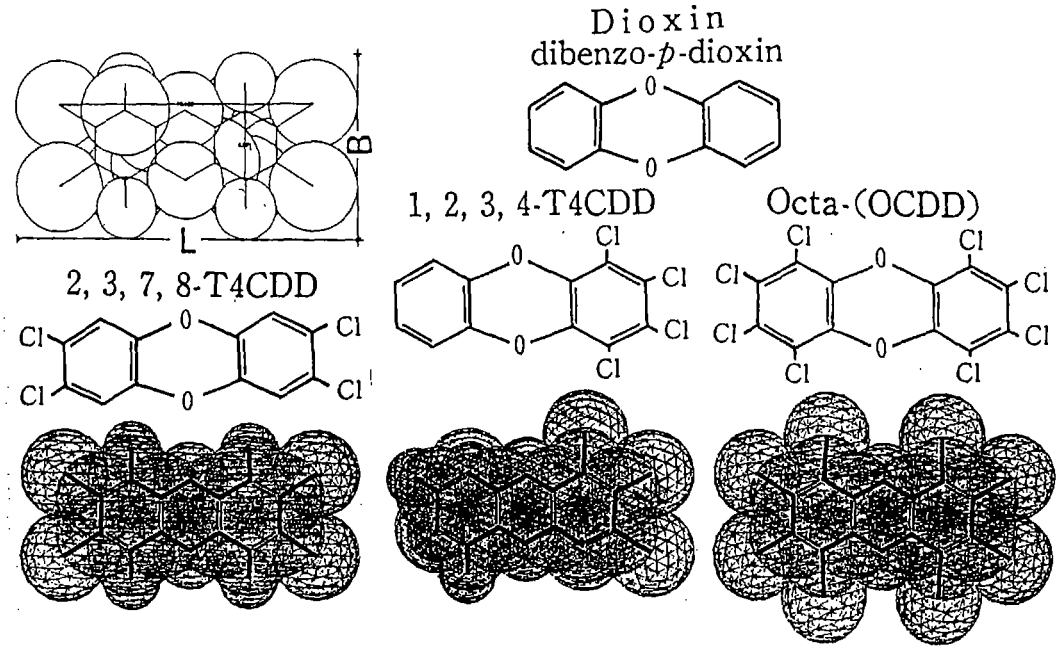
Table I Amounts of PCDDs and PCDFs in Flyash from Gas Works in Dalian

compound	pg/g flyash
H4CDDs～H6CDDs	nd*
H4CDFs～H6CDFs	nd*
total H7CDDs	68.5
1,2,3,4,6,7,8-H7CDD	29.9
total H7CDFs	313.4
1,2,3,4,6,7,8-H7CDF	58.2
1,2,3,4,7,8,9-H7CDF	49.1
OCDD	69.3
OCDF	562.2

*nd:not detected

Table II Calculated L/B Ratios of Dioxins

compound	length(L) Å	breadth(B) Å	L/B ratio
dibenzo-p-dioxin	11.511	7.403	1.555
1,2,3,4-T4CDD	12.411	8.086	1.538
2,3,7,8-T4CDD	13.621	7.367	1.849
OCDD	13.742	9.758	1.408



the gas works showed the presence of 29.9pg of 1,2,3,4,6,7,8- H7CDD, 58.2 pg of 1,2,3,4,6,7,8-H7CDF, and 49.1pg of 1,2,3,4,7,8,9-H7CDF. It was very interested in that no detection of 4,5,6,7,8-CDD and 4,5,6,7,8-CDF resulted in all flyash samples from the coal-burning steam-engines of locomotives.

Liquid crystal stationary phases have been observed to provide a shape selective aspect to chromatographic separation such that geometrical and positional isomers eluted in an order that approximately follows thier length-to-breadth ratio(L/B) and planarity. The L/B ratios of dibenzo-p-dioxin, 1,2,3,4-T4CDD, 2,3,7,8-T4CDD and OCDD were calculated with a Sony-Tektronix computor, as shown in Table II.

The chromatographic behaviors of the separation on columns using newly synthesized liquid crystals as a stationary phase, were discussed with the GC retention behaviors and graphical shapes in the following figures of the structures of the four compounds.

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3 Albrecht, I.D., Naikwadi, K.P., Karasek, F.W., Hatano, H.; Anal. Sci., 1991; 7: 215-8
4 Beard, A., thesis for Ph. D., 1991; Univ. of Waterloo.
5 Preliminarily Posting; Tokyo: 1991: 25th Ann. Meeting Japanese Anal. Chem. Soc., Nov.23: 3P23