EFFECTS OF TEMPERATURE AND DEHP(DI-(2-ETHYLHEXYL) PHTHALATE) ON THE POLYCHLORODIBENZO-*P*-DIOXINS AND DIBENZOFURANS(PCDDs/PCDFs) FORMATION IN NATURAL SEA SALT BY USING FOOD ADDITIVE

Ki Cheol Kim, Jae Kwan Kim, Myung Jin Lee, Young Suk Kim, Hoan Uck Ko, Chin Suk Son and Yoon Chang Park*

Gyeonggi-do Institute of Health & Environment research, 324-1 Pajang-dong, Jangan-gu, Suwon, Gyeonggi-do, 440-290, Korea
*Analytical Chemistry, Sungkyunkwan University, 300 chunchun-dong, Jangan-gu, Suwon, Gyeonggi-do, 440-290, Korea

Introduction

Major environmental sources of PCDDs/PCDFs formation have been known for the combustion of waste materials in terms of the high-temperature process. There have been many studies on lots of dioxin formation under various conditions[1, 2]. But the dioxin formation mechanisms are not fully understood yet because many complex reactions might be involved in the process. The doxin formation through the high-temperature process will be applied to the food in some cases.

The natural sea salt is the basic material of all food in dietary life. Also oriental countries such as Korea have used the salt made out of the high-temperature process since the early times. The high-temperature process shows that infinitesimal organic materials on natural sea salt are able to react with HCl(g), Cl^- or $Cl\cdot$ radicals due to sodium chloride(NaCl) and furthermore indicates that poisonous compounds such as poly chlorodibenzo-*p*-dioxins and dibenzofurans(PCDDs/PCDFs) are formed. Because of cronic and acute health effects of PCDDs/PCDFs, it is important to determine, even extremely low levels[3], how much dioxins form from natural sea salt in the high-temperature processes in order to reduce their role in food contamination.

Meanwhile it is also important to know what compound acts by the precursor material of dioxin formation in the high-temperature process. In this regard, DEHP(di-(2-ethylhexyl)phthalate) is able to act by dioxin formation precursors in the high-temperature process because of including benzyl group in DEHP. This phtalate ester compound, known to be substances of low toxicity, is ubiquitous pollutant in the environment owing to its widespread use as plasticizer in the plastics fabricating industry [4].

The aims of this paper are to present and discuss the levels of PCDDs/PCDFs in the processed salt treated in the high temperature and to investigate the distributing characteristic of PCDDs/PCDFs. The natural sea salt alone and the natural sea salt added DEHP compound were treated with the high-temperature process from 250 to 750 during 2 hours. The samples were analyzed for PCDDs/PCDFs by gas chromatography/mass spectrometry.

Methods and Materials

Isotope-labeled dioxins for internal standard, sampling-spike recovery test and clean up spike recovery test were purchased from Cambridge Isotope Laboratories, Inc.(USA). All organic solvents used in extraction and clean-up process were of pesticide grade and obtained from Wako Chemical Co.(Japan). Samples of natural sea salts purchased from a local supermarket in Suwon, South Korea.

In the first place, natural sea salts were processed by high temperature in electric furnace from 250 to 750 at intervals of 100 during 2 hours. The samples were extracted and cleaned up by using modified EPA method 1613. Figure 1 shows the flowchart of extraction and clean-up procedure.

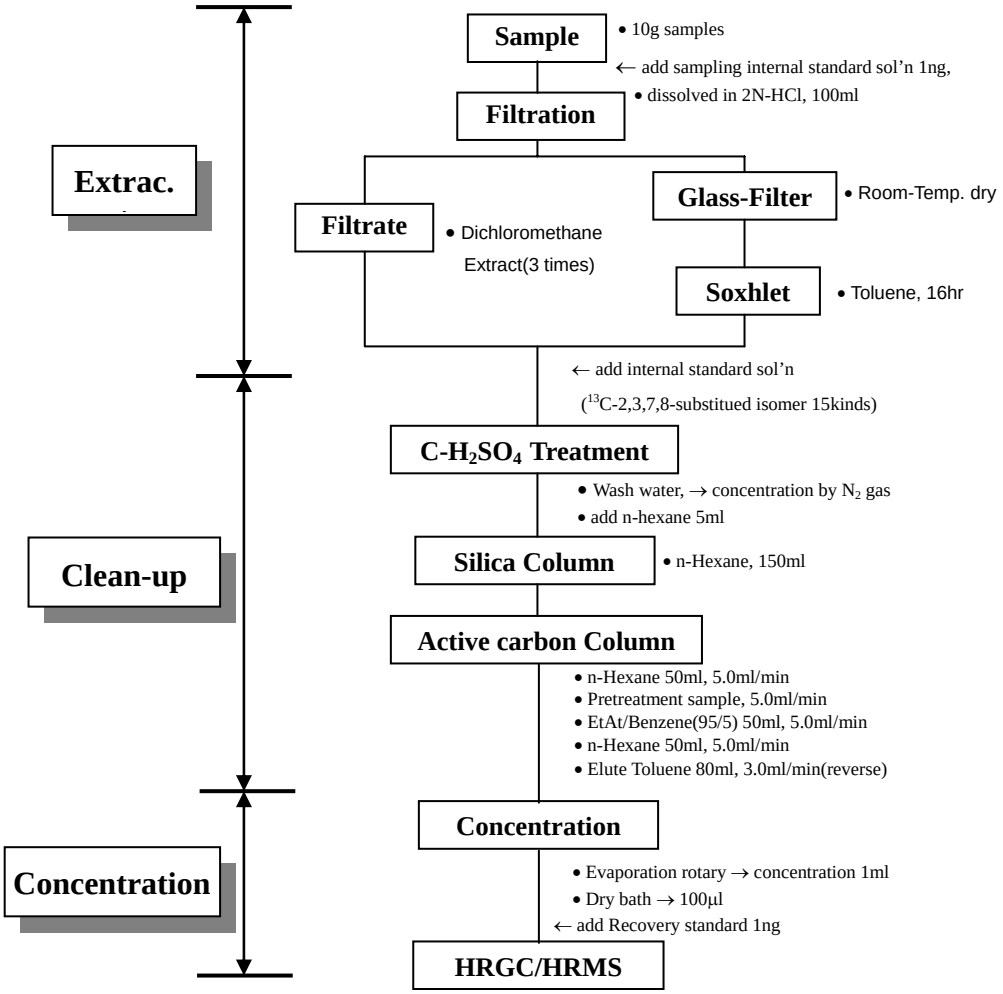

Fig. 1 Flowchart of extraction and clean-up procedure of samples

All analysis was performed in a way of using an GC 8000series(Fisons Instruments, Italy) equipped with a CTC 200S autosampler and an Autospec Ultima Mass Spectrometer(Micromass, UK) that was operated in the voltage selected ion recording mode at resolutions greater than 10,000RP(10% vally definition).

Results and Discussion

The temperature effect of dioxin formation was studied at 250 , 350 , 450 , 550 , 650 , 750 . Table 1 shows the levels of PCDDs/PCDFs of the each sample. PCDDs/PCDFs formation in the high temperature was most generated in near of 450 and then the total amount of dioxins was 90.07pg/g (6.07pgTEQ/g). These results show considerably higher values than in natural salt. The amount of dioxin formed in baked salt according to the number of chlorides was Cl_5>Cl_6>Cl_7>Cl_8>Cl_4 in PCDD isomers and Cl_6>Cl_5>Cl_4>Cl_7>Cl_8 in PCDF isomers. PCDF isomers composed over 90% of the total dioxins formed at 450 . Figure 2 shows characteristic profile of PCDDs/PCDFs homologue formed by raising temperature. The result presents that the formation of dioxins rapidly decrease at temperature above 550 .

Table 1. The levels of PCDDs/PCDFs of the natural sea salts processed by heating

Sample	PCDDs		PCDFs		Total Dioxins	
	pg/g	pg TEQ/g	pg/g	pgTEQ/g	pg/g	pg TEQ/g
Natural sea salt	ND	ND	0.3202	0.022	0.3202	0.022
250	0.07	0.043	0.13	0.025	0.20	0.068
350	0.72	0.048	1.62	0.137	2.34	0.185
450	6.41	0.369	83.66	5.701	90.07	6.070
550	2.47	0.103	34.43	0.958	36.90	1.061
650	0.16	0.0002	0.47	0.02	0.63	0.020
750	0.25	0.058	ND	ND	0.25	0.058

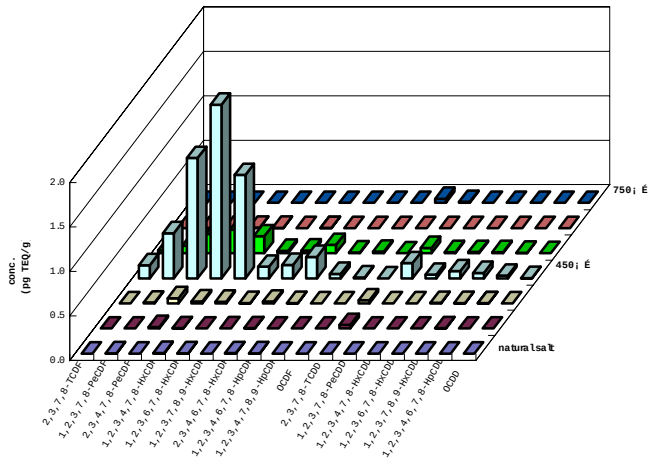

Fig. 2 Influence of the temperature on Homologue distribution of PCDDs/PCDFs formed In natural sea salt (Temp. variation: 250 - 750 , 2hours)

Table 2 shows the levels of PCDDs/PCDFs as formed by adding DEHP and heating. Dioxin

formation of dioxins is increased in proportion to additive DEHP. PCDD isomers are remarkably increased as compared with PCDF isomers. Total PCDFs/PCDDs concentration is 512.30pg/g (21.53pg TEQ/g) in case of adding 100mg of DEHP. This value is above three times compared with natural sea salt processed by heat(450 , 2hrs). This result indicates that DEHP, a kind of aromatic compound, is one of the dioxin formation precursors in the high-temperature process. Figure 3 shows the characteristic profile of PCDDs/PCDFs homologue as formed by adding DEHP and raising temperature.

Table 2. The levels of dioxins originated by adding DEHP and heating for natural sea salt

Sample	PCDDs		PCDFs		Total Dioxins	
	pg/g	pg TEQ/g	pg/g	pg TEQ/g	Pg/g	pgTEQ/g
natural sea salt	ND	ND	0.320	0.022	0.322	0.022
baked(450 , 2hr)	69.54	2.24	77.96	6.11	147.50	8.35
DEHP(10mg) + baked	92.92	2.59	62.73	4.94	155.65	7.53
DEHP(100mg) + baked	445.95.	14.38	66.35	7.15	512.30	21.53

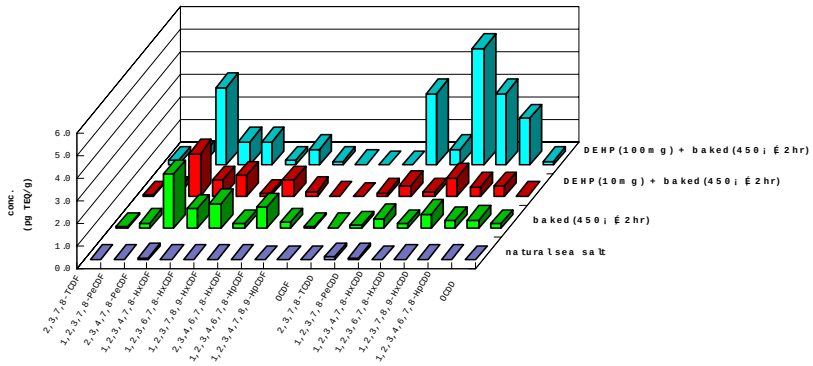

Fig. 3 Influence of adding DEHP and raising temperature on Homologue distribution of PCDDs/PCDFs formed in natural sea salt

In this study, the reaction factors for PCDD/PCDFs formation suggest that the heating process of salt can generate HCl(g), Cl_2(g) or active radicals. These chlorine compounds can react with infinitesimal organic compounds including aromatic ring such as DEHP and make an organochlorine compounds such as PCDD/PCDFs.
However further investigations are needed to elucidate the mechanism of PCDDs/PCDFs originated by adding DEHP and heating process.

Reference

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