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DEVELOPMENT OF ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR DERIVATIVES BY HRGC-HRMS, AND THE REAL SITUATION OF ENVIRONMENTAL POLLUTANTS FROM WASTE INCINERATOR

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are generated mainly by incomplete combustion of petroleum derived products. On the other hand, nitro-substituted polycyclic aromatic hydrocarbons (Nitro-PAHs) have been found in automobile emissions, ambient air, and other industrial processes¹⁾. Nitro-PAHs are strongly mutagenic in the Salmonella test and some of them are carcinogenic in the long-term test on animals. Many studies revealed that in daytime in the atmosphere, gaseous PAHs reacts with hydroxyl radical ($\cdot\text{OH}$) followed by addition of nitrogen dioxide (NO_2) for the generation of Nitro-PAHs and then Nitro-PAHs are decomposed with a loss of H_2O from their molecule²⁾.

By the way, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) are called as dioxin related compounds (DXNs), which all are a kind of PAHs. Many countries including Japan have made efforts to reduce DXNs released from the municipal waste incinerator. The measure of control is the improvement of combustion conditions such as combustion and boiler technologies. Especially, the technique of high temperature burning is the most effective for the reduction.

However, the technique has a possibility that the formations of nitrogen oxide (NO_x) and Nitro-PAHs will increase due to high temperature burning.

Therefore, in this study, we developed a newly analytical method of PAHs and Nitro-PAHs, and surveyed a real situation of their emission from municipal and industrial waste incinerators.

Materials and Methods

Table 1 shows operating conditions of tested 10 incinerators. Flue gas samples were obtained from these incinerators according to a modified method of JIS Z 8808 (Japanese Industrial Standard)³⁾.

DXNs in the flue gas specimen were analyzed according to our previous report⁴⁾. Finally, the

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purified extracts were dissolved in n-decane and analyzed for DXNs on EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 6890 gas chromatograph-JEOL 700M mass spectrometer according to our report⁴⁾.

PAHs in the flue gas were analyzed using U.S. EPA method TO-13 with a minor modification. An aliquot (0.1 ml) of the extract was spiked with a mixture of five deuterium labeled compounds (Naphthalene, Acenaphthene, Phenanthrene, Chrysene and Perylene). The solution was cleaned up on silica gel column (Merck, Kieselgel 60, 60-230 mesh, 10 g, activated on 3 hr at 130°C) with an eluent of 50% CH₂Cl₂/n-hexane (100 ml). The eluate containing PAHs was concentrated up to 3 ml. After addition of 20 µl of n-decane as a keeper solvent, the concentrate was left for complete evaporation of the rest solvent in room temperature and then adjusted to a volume of 20 µl with n-decane.

PAHs and Nitro-PAHs were analyzed on a SGE BPX-5 capillary column (30 m × 0.25 mm, 0.25 µm) (held for 1 min at 45°C, programmed for 45°C to 200°C at 30°C/min and to 320°C at 7°C/min, and held for 1.5 min) on EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 6890 gas chromatograph-JEOL 700M mass spectrometer.

Development of analytical procedure for Nitro-PAHs

An acid-base partitioning method was adapted for purification of Nitro-PAHs in the flue gas sample by Sellstrom et al⁵⁾. However, we revealed that the method had some faults such as a low recovery of internal standards and a complexity etc. Therefore, we developed a newly purified method using silica gel column chromatography. On the other hand, Nitro-PAHs were analyzed as follows. The extract of flue gas was cleaned up on a 0.5%(w/w) AgNO₃/silica gel (3 g) with the first eluent of n-hexane (100 ml) and the second eluent of 50% CH₂Cl₂/n-hexane (100 ml). The second eluent was concentrated finally dissolved with 20 µl of n-decane and analyzed for Nitro-PAHs on a SGE BPX-5 capillary column by HRGC/HRMS.

Results and discussion

The first examination was done about a comparison between purification techniques of an acid-base partitioning method⁵⁾ and a silica gel column chromatography for Nitro-PAHs. The acid-base partitioning method showed low recoveries of standards with only 13 to 31% and insufficient removal of impurities. On the other hand, 0.5% AgNO₃/silica gel column chromatography was a simple method and a good stable recovery of standard with a range of 79 to 113%. In addition, it was revealed that the AgNO₃/silica gel is an excellent for removal DXNs from PAHs and Nitro-PAHs, showing the agent to more strongly adsorb the latter than the former. We investigated a real situation of environmental pollution by DXNs, PAHs and Nitro-PAHs from the flue gas of the municipal and industrial waste incinerators.

Table 1 shows the type of tested incineration facility, combustion temperature, main contents of

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waste, and capacity of waste combustion. The concentration of DXNs ranged from 3.2 to 7300 ng/m³N, while the TEQ concentration ranged from 0.044 to 160 ngTEQ/m³N. Compared to batch type industrial incinerators (A, B and E), the level of DXNs of mechanization batch type and semi continuation type incinerators (F, G, H, I and J) were relatively low. It is well known that the generation of DXNs is reduced under a condition of high temperature combustion. However, contrary to this, it was expected that the condition might promote the formation of nitric oxide (NO_x) and consequently elevate the generation of Nitro-PAHs, which are produced by substitution of a nitro group in PAHs.

As shown in Table 2, PAHs and Nitro-PAHs were detected from all samples. Their levels were in ranges of 0.55 to 53 µg/m³N for PAHs and 3.0 to 270 µg/m³N for Nitro-PAHs, respectively. The main compounds of PAHs were naphthalene, phenanthrene, fluoranthene, pyrene, chrysene and benzo(a)pyrene. On the other hand, nitrophenanthrene and nitrochrysene were found as common Nitro-PAHs to most incinerators. The concentration of phenanthrene and chrysene occupied for the most of total PAHs. Therefore, this might result in producing of nitrophenanthrene and nitrochrysene as majors of Nitro-PAHs. We considered that the formations of PAHs and Nitro-PAHs might be effected to the concentrations of CO and O₂. In previous reports, it was already found that the CO concentration became higher, and the PAHs formation increased greater. Therefore, we had an interest in a correlation between the levels of Nitro-PAHs and CO. In fact, in the case of CO level over 50 ppm, PAHs and Nitro-PAHs were high concentration. On the other hand, it was clear that CO and combustion temperature influenced about emission of DXNs. Moreover, the emission of DXNs were controlled with high temperature burning, the levels of PAHs and Nitro-PAHs showed roughly a decrease tendency. However, an incinerator A with a low combustion temperature with 420 to 650°C showed a high level of 7300 ng/m³N for DXNs and a low level of 19 µg/m³N for Nitro-PAHs, respectively.

As shown in Table 2, this study also revealed that incineration facilities such as industrial incinerator and small-scale incinerator with a sufficient combustion control released largely PAHs, Nitro-PAHs and DXNs to the atmosphere.

References

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Table 1 Operating conditions of various incinerators in this research

	Type of facility	Temp. (°C)	Content	Ability of incineration (ton/hr)
A	Batch	420-651	Building materials	30 ton/day
B	Batch	700-800	Building materials	-
C	Small incinerator	800-1000	Municipal solid waste	0.18
D	Small incinerator	600-1000	Corrugated cardboard	0.75 ton/day
E	Batch	600-850	Wood chip, Paper dust	0.19
F	Mechanization, Batch	800-930	Municipal solid waste	7.0 ton/day
G	Mechanization, Batch	770-820	Municipal solid waste	7.0 ton/day
H	Semi continuation, Batch	850	Municipal solid waste	3.8
I	Semi continuation, Batch	880-910	Municipal solid waste	3.8
J	-	1000	Municipal solid waste	0.5

Table 2 Amounts of DXNs, PAHs and Nitro-PAHs in flue gas from various incinerators

		A	B	C	D	E	F	G	H	I	J
O ₂ (%)		12.6	6.9	13.6	12.9	11.2	12.5	13.5	15.3	14.8	20.7
CO (ppm)		86	289	476	18	299	11	10	14	7	27
DXNs (ng/m ³ N)*		7300	3500	250	220	81	72	42	9.7	3.2	0.79
DXNs TEQ (ngTEQ/m ³ N)**		160	74	5.0	4.8	1.4	1.1	0.69	0.13	0.044	0.36
2 rings PAH (µg/m ³ N)		0.042	0.37	0.85	0.12	0.23	0.47	0.058	0.60	0.80	0.040
3 rings PAH (µg/m ³ N)		0.066	19	2.3	0.054	3.8	0.13	0.027	0.031	0.039	0.10
4 rings PAH (µg/m ³ N)		0.41	33	11	0.19	4.9	0.95	0.40	0.10	0.097	0.13
5 rings PAH (µg/m ³ N)		0.27	1.0	0.91	0.18	0.42	0.69	0.44	0.30	0.30	0.28
Total PAHs (µg/m³N)		0.79	53	15	0.55	9.4	2.2	0.92	1.0	1.2	0.56
Mononitro-PAH (µg/m ³ N)	2 rings	0.071	12	6.7	0.015	4.1	0.10	0.10	0.012	N.D.	0.02
	3 rings	2.9	220	44	2.0	7.0	6.2	3.7	1.3	1.9	3.7
	4 rings	N.D.	N.D.	N.D.	0.85	8.7	5.1	4.6	1.7	5.1	3.1
	Total	3.0	230	51	2.8	20	11	8.3	3.0	7.0	6.8
Dinitro-PAH (µg/m ³ N)	2 rings	0.34	34	3.5	0.16	3.2	0.42	0.061	0.01	N.D.	0.029
	3 rings	11	N.D.	40	2.1	12	1.1	0.49	N.D.	N.D.	N.D.
	4 rings	5.2	N.D.	9.1	2.4	7.3	0.26	0.039	N.D.	N.D.	N.D.
	Total	16	34	53	4.6	22	1.8	0.59	0.01	N.D.	0.029
Total Nitro-PAHs (µg/m³N)		19	270	100	7.5	42	13	8.9	3.0	7.0	6.8

*: DXNs (ng/m³N): actual concentration

** : DXNs (ngTEQ/m³N): TEQ concentrations were calculated from Toxicity Equivalency Factor (WHO-TEF)

2 rings PAH: Naphthalene, 2-Methylnaphthalene; 3 rings PAH: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene;

4 rings PAH : Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene ; 5 rings PAH: Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene

Mononitro-PAH : 1-, 2-nitronaphthalene, 2-, 3-, 4-nitrobiphenyl, 3-Nitrodibenzofuran, 9-Nitroanthracene, 3-, 4-Nitrophenanthrene, 7-Nitrobenzo(a)anthracene, 6-Nitrochrysene ; Dinitro-PAHs : 1,3-, 1,5-, 1,8-Dinitronaphthalene, 2,2'-Dinitrobiphenyl, 1,3-, 1,6-, 1,8-Dinitropyrene, 2,7-Dinitrofluorene, 9,10-Dinitroanthracene

N.D.: Not detected (<0.01 µg/m³N)