

Efficient and Economical Measuring Method of PCDDs/Fs for Flue Gas

Yutaka Nagayanagi, Yoshihiro Saito, Akira Aono, Jun Nagata, Mika Kato*, Kohei Urano* and Haruhisa Syudo**

Shimadzu Corporation, 3, Kanda-Nishikicho 1-Chome, Chiyoda-ku, Tokyo, Japan

*Yokohama National University, Laboratory of Safety and Environmental Engineering,
79-5, Tokiwadai, Hodogaya-ku, Yokohama, Japan

**NEDO(New Energy and Industrial Technology Development Organization)

Sunshine 60, 29F, 1-1, 3-Chome Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan

Introduction

The measurement of PCDDs/Fs in flue gas is socially required because incineration is the main source of PCDDs/Fs in most of countries. But it is necessary much cost and highly skill to measure PCDDs/Fs. Especially, the cost of the measurement is important for the countermeasure of PCDDs/Fs when many incinerators are distributed throughout the country like Japan. Since the TEQ value is mostly the target to evaluation, every 17 toxic isomers must be determined separately. Therefore, the expensive HRGC/HRMS is the necessary instrument to avoid the interference of other compounds.

We developed efficient sampling method of PCDDs/Fs in flue gas and sensitive determination technique by economical HRGC/LRMS.

Materials and Methods

The measuring method consists of four major steps, those are, sampling, extraction, cleaning-up and determination steps.

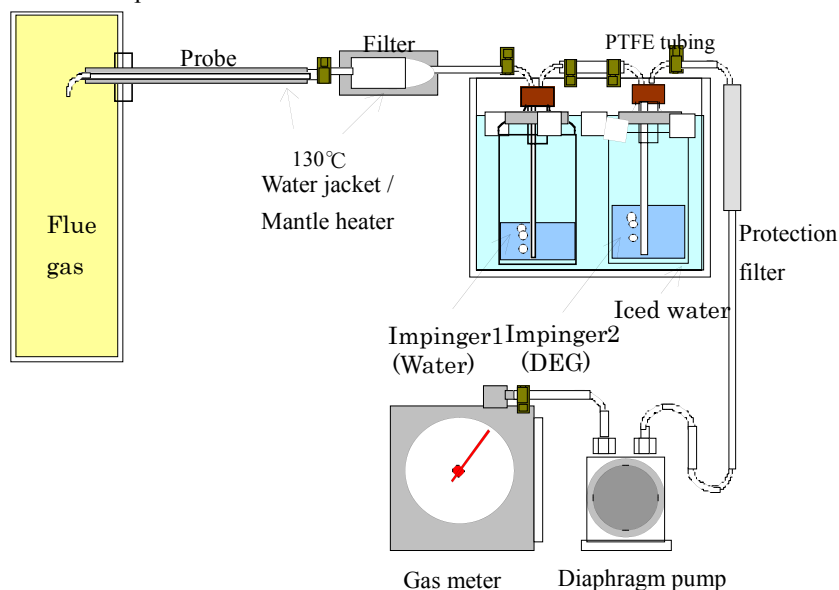


Fig.1 Developed Sampling System

The developed sampling system consisted of two impingers is shown in Fig.1. PCDDs/Fs in flue gas were condensed in the first impinger with 200mL water and absorbed in the second impinger with 200mL or 300mL diethylene glycol (DEG) in a cooling box. The sampling probe will be cooled by water jacket or heated by mantle heater to the gas temperature ca. 130°C. The cylindrical filter can be omitted when the concentration of dust is low as in recent incineration facilities. When the condensed water is estimated more than capacity of the first impinger, an empty bottle will be added before the first impinger. The extraction procedure can be simplified when the filter is not used.

The filter is quickly extracted with toluene by using an ultrasonic bath. But when the sample contains large amount of soot or carbon dust, another extraction method like as Soxhlet extraction etc. must be used. The extract sample was cleaned-up by a sulfuric acid-silica column and a HPLC system. The cleaned-up sample is analyzed sensitively with a bench top HRGC/LRMS by PTV (Programmable Temperature Vaporizer) method.

Results and Discussion

Sampling efficiency of the PCDDs/Fs by the developed sampling system

The recoveries are examined by using an additional XAD resin adsorber and second impinger with DEG for recovering leakage, and the results are shown in Table 1. Enough recoveries with the two stage impingers were confirmed after RUN 4 when appropriate modification was taken for effective cooling with enough ice and also for proper contact of gas with 300mL DEG in the second impinger. Therefore, it was confirmed that the developed sampling system composed the two impingers containing 200mL water and 300mL DEG could recover PCDDs/Fs completely.

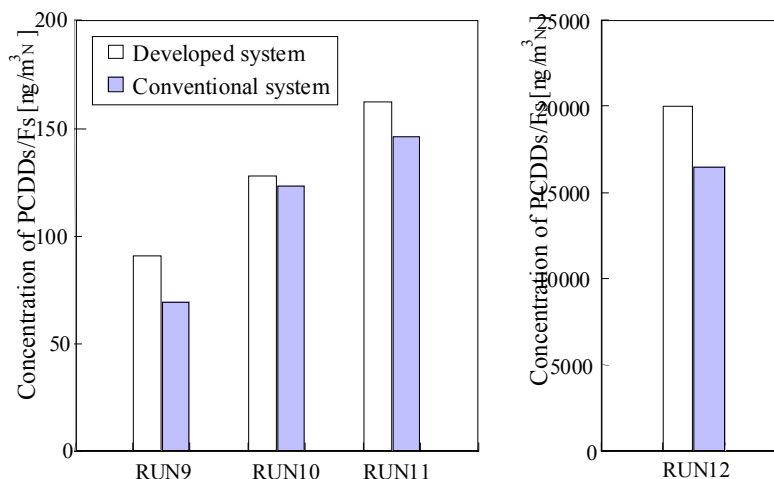
Table 1 Recovery of PCDDs/Fs by the developed sampling system

	[ng/m ³ _N]							
	RUN1	RUN2	RUN3	RUN4	RUN5	RUN6	RUN7	RUN8
Water and diethylene glycol (developed system)	87	123	425	76	4608	6030	3005	820
XAD resin and second diethylene glycol (after developed system)	4	5	79	0.0	0.0	0.0	0.0	0.0
Total	91	128	505	76	4608	6030	3005	820
Recovery by developed system [%]	96	96	84	100	100	100	100	100

RUN1 - 3 : 200mL DEG, RUN4 - 8 : 300mL DEG

Comparison of measured values by developed and conventional sampling systems

The data measured instantaneously by the developed sampling system and the conventional Japanese system which uses a filter, two water impinger, a XAD resin adsorber, a DEG impinger and an empty bottle were compared, and the results are shown in Fig.2. It shows that developed system could get same or higher values than those by the conventional system. Furthermore, same results were confirmed by three companies of analysis. And the analytical data of PCDDs/Fs isomers in the same extracted samples by a company and our laboratory are shown in Table 2. The



data of each isomer by the both laboratories agreed well.

Table2 Comparison of analytical data of PCDDs/Fs isomers in the same extracted samples by a company and our laboratory

	[ng-TEQ/m ³ N as O ₂ =12%]						
	RUN13		RUN14		RUN15		
I-TEF	Our Lab.	CompanyA	Our Lab.	CompanyA	Our Lab.	CompanyA	
2,3,7,8-T4CDD	1.00	3.0	2.8	5.3	3.5	0.94	1.1
1,2,3,7,8-P5CDD	0.5	7.3	6.5	9.0	7.0	2.6	2.1
1,2,3,4,7,8-H6CDD	0.1	0.79	0.80	0.72	0.67	0.26	0.21
1,2,3,6,7,8-H6CDD	0.1	1.1	1.2	0.92	0.88	0.32	0.27
1,2,3,7,8,9-H6CDD	0.1	0.95	0.70	0.62	0.53	0.20	0.16
1,2,3,4,6,7,8-H7CDD	0.01	0.17	0.17	0.17	0.15	0.079	0.071
1,2,3,4,6,7,8,9-O8CDD	0.001	0.0038	0.0054	0.0051	0.0041	0.0040	0.0035
Total PCDDs-TEQ		13.4	12.2	16.7	12.7	4.36	3.87
2,3,7,8-T4CDF	0.1	4.9	2.8	3.5	3.5	1.2	1.1
1,2,3,7,8-P5CDF	0.05	4.2	3.7	3.7	3.4	1.2	1.1
2,3,4,7,8-P5CDF	0.5	32	29	33	27	7.8	7.0
1,2,3,4,7,8-H6CDF	0.1	5.1	4.9	4.4	3.9	1.1	1.0
1,2,3,6,7,8-H6CDF	0.1	5.1	5.2	4.2	4.3	1.1	1.1
1,2,3,7,8,9-H6CDF	0.1	0.32	0.31	0.45	0.23	0.089	0.06
2,3,4,6,7,8-H6CDF	0.1	4.2	4.3	3.2	3.2	0.92	0.97
1,2,3,4,6,7,8-H7CDF	0.01	0.74	0.73	0.60	0.62	0.22	0.20
1,2,3,4,7,8,9-H7CDF	0.01	0.049	0.047	0.057	0.053	0.024	0.025
1,2,3,4,6,7,8,9-O8CDF	0.001	0.0028	0.0026	0.0046	0.0031	0.0043	0.0025
Total PCDFs-TEQ		53.2	50.4	52.5	45.7	13.5	12.5
Total PCDD/Fs-TEQ		67	63	69	58	18	16

Fig.2 Comparison of measured values for the same flue gas by developed and conventional sampling systems

High sensitive determination technique in HRGC/LRMS

The sensitivity of HRGC/LRMS is not so high as HRGC/HRMS, but the sensitivity could be enhanced by increasing the sampling volume of flue gas and the injection volume into the GC/MS by the PTV method.

Figs.3 and 4 show the good linearity in peak areas with injection volumes up to 20 microliters, when we use the PTV injection method for a HRGC/LRMS of Shimadzu type QP5000.

By using the HRGC/LRMS, the instrument cost can be reduced drastically, and also the training cost for the operator and the maintenance cost can be reduced.

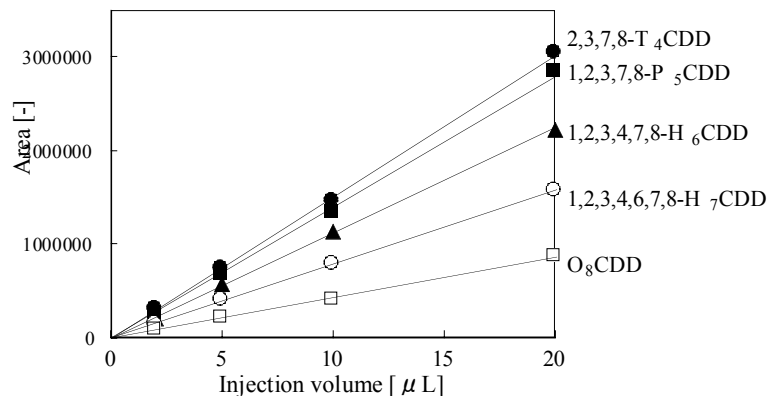


Fig.3 Relationships between peak areas of PCDDs and injection volumes into GC/MS
(Concentration of PCDDs: 25pg/ μL)

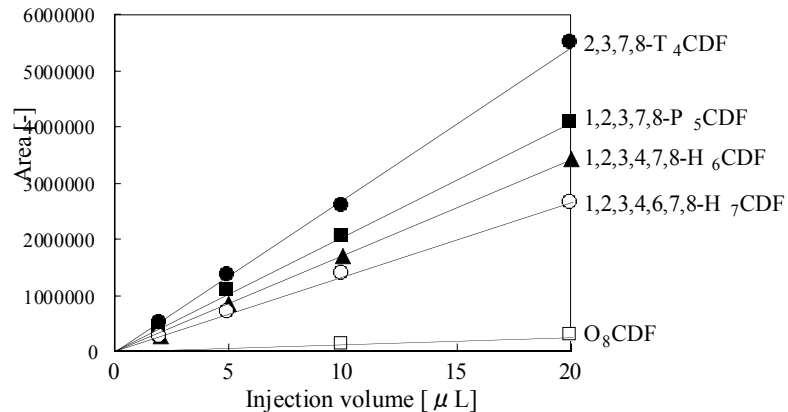


Fig.4 Relationships between peak areas of PCDFs and injection volumes into GC/MS
(Concentration of PCDFs: 25pg/ μL)

The developed measuring method could be reduced drastically with the operation time, the use

solvent volume, and cost. It gives realistic method for routine analyses especially for the flue gas of various incineration facilities.

Acknowledgment

This study was supported by MITI(Ministry of International Trade and Industry) and NEDO(New Energy and Industrial Technology Development Organization).