

## ANALYSIS OF CHLOROPHENOLS IN FLUE GAS OF WASTE INCINERATORS BY HPLC/ECD INSTALLED IN SEQUENTIAL AUTOMATED MONITORING INSTRUMENT AS WELL AS BY HPLC/MS AND GC/MS

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### Introduction

Chlorophenols (CPs) in flue gas from waste incinerators are noted as the precursors of PCDDs (Polychlorinated Dibenzop-dioxins) and PCDFs (Polychlorinated Dibenzop-furans). In addition, some of CPs are relevant to environmental endocrine disrupters. Thus, the monitoring of CPs in flue gas is very important. However, CPs are easily soluble into the condensed water (CW), which is usually very abundant in flue gas from waste incinerators. The analysis of CPs by GC or GC/MS needs extraction process, then, the automated analysis by GC, which is most common in monitoring VOCs, becomes complicated. In this study, we selected HPLC with an electrochemical detector (ECD), which has high selectivity and sensitivity to CPs<sup>1</sup>, and developed two types of the sequential automated monitoring instrument by using HPLC/ECD analysis of the solution collecting CPs in flue gas with a cooled trap. The analytical data obtained from HPLC/ECD were compared with the values from HPLC/MS and chemical derivatization (CD)-GC/MS

### Methods, Instrument and Materials

#### *HPLC/ECD (Manual and auto mode)*

We already confirmed the detection of CPs in flue gas by HPLC/ECD<sup>1</sup>, then the analytical instrument and conditions taken here are similar to our earlier experiment.

**HPLC**; GL Sciences INC, LC 600. Sample injector; RHEODYNE 7125, 0.5mL (manual).

Analytical and pre column; GL Sciences INC, Inertsil ODS-3(10cm, 2.1mm I.D., 3µm).

Eluent: 0.2ml/min [methanol]/[0.5% phosphoric acid]=60/40 at 35°C.

**ECD**; GL Sciences INC, ED 623. Glassy carbon (manual) or diamond (auto) working electrode applied at 1.2V (manual) or 1.3V (auto) vs. Ag/AgCl.

Data processor; EZ Chrom Elite (Ver.2.61).

#### *HPLC/MS*

HPLC/MS have been widely used<sup>2)</sup> and provides the data to check the peaks in chromatograms by HPLC/ECD with similar column conditions.

**HPLC**; Hewlett Packard Co.- series 1100, with the similar analytical condition described in Sec. 2.1.

**MS**; Micromass Co.- Quattro LC

Ionization method; Electro spray ionization (ESI, negative mode).

Ion source temp.; 110 °C.

Detection method; MRM.

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Table 1. Fragment ions used for detection, m/z

	Parents	Daughter
Di-CP	160.9	125.0
Tri-CP	194.9	159.0

Table 2. Fragment ions used for detection, m/z

	Detection ion	Quantity ion
Di-CP	164	162
Tri-CP	198	196
	---	192

\* 2-Bromo-4-fluorophenol acetate

## Chemical derivatization (CD)-GC/MS

We used the direct acetylation CD process for CPs analysis before GC injection because of the reliable results. The analytical procedures and conditions taken here are similar to our earlier experiment<sup>3)</sup>.

1. Add purified water 97.5 mL into sample CW 2.5 mL.
2. Add potassium carbonate 0.5 g, acetic anhydride 1 mL (Direct acetylation CD).
3. Extract it by dichloromethane twice (20 and 10 mL) and pool them.
4. Add the standard solution (2-bromo-4-fluorophenol acetate) into the extract.
5. Dehydrate the extract and condense it.
6. Inject the condensed extract into GC/MS

### GC; Trace GC

Carrier gas; He (1mL/min)

Analytical column; Restek Co. Rtx-5MS (30m × 0.25mm i.d. × 0.25µm film)

Column temp; 50 °C(1min) - (5 °C/min) - 200 °C

Injection; 2µL with splitless at 200°C

### MS; Thermo Quest Co. Trace MS

Temp. for the interface and ion sources; 250 °C and 200 °C

Detection mode for MS; SIM (Selected Ion Monitoring)

## Results and Discussion

### Basic examination of three methods for CPs analysis

The toxic PCDDs/-Fs have four or more chlorine atoms and the CPs, the precursors, having two or more chlorine atoms seems to be important, and these 11 compounds shown in Table 3 were the major targets for analysis. The determination limit (DL) and relative sensitivity (RS) of CPs by three methods were estimated and shows in Table 3. HPLC/ECD has highest sensitivity among three methods. DL and RS of CPs by HPLC/MS are widely varied with the compounds, however the analytical processes are very simple as HPLC/ECD. CD-GC/MS has high sensitivity and relatively uniform sensitivity to most of the tested CPs, however the analytical processes are rather complicated.

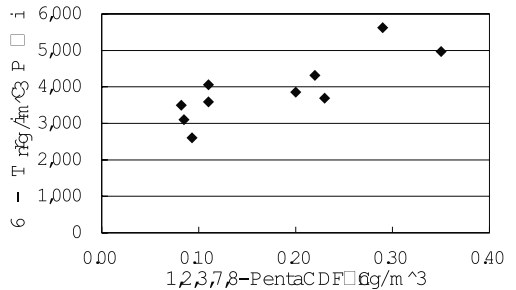
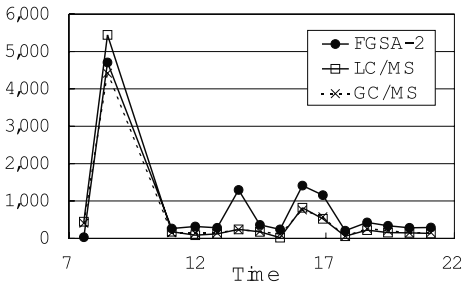
### Comparison of the analytical results of CPs in flue gas by three methods

The solution (0.5% phosphoric acid) 5mL for collection of CPs in flue gas was poured into the trap cooled with ice water before sampling. The solution volume was increased with the drain water condensed from the vapor (20-30 %, v/v) in flue gas and reached to 15- 20 mL after the sampling of 50-100 L flue gas. We confirmed that the efficiency for each CPs collection with the absorption solution (AS), which was composed from 5mL of phosphoric acid and 10-15 mL of the condensed water in the cooled trap, were mostly 100%.

**Table 3.** Determination limit and relative sensitivity for chlorophenols by three methods

	HPLC/ECD		HPLC/MS		CD-GC/MS	
	DL*	RS**	DL*	RS**	DL*	RS**
2,3-DiCP	5	1.2	239	2	12	0.8.
2,4-DiCP	7	1.0***	28	10***	10	1.0
2,5-DiCP	7	1.0	95	5	10	1.0
2,6-DiCP	4	1.6	921	0.5	11	0.9
3,4-DiCP	7	1.1	2	291	10	1.1
3,5-DiCP	8	1.3	3	245	11	0.9
2,3,4-TriCP	17	0.6	8	107	18	0.6
2,3,5-TriCP	16	0.8	71	13	18	0.6
2,3,6-TriCP	10	0.9	35	21	18	0.6
2,4,5-TriCP	20	0.6	12	74	15	0.8
2,4,6-TriCP	20	0.6	7	138	14	0.8

Note, \*DL : Determination Limit (pg/mL, S/N=3). \*\*RS : Relative Sensitivity.  
\*\*\* : Standard for reference.



**Figure 1.** 2,4-DiCP by three methods from start to stop of the incinerator “C”, Nov. 15, 2001

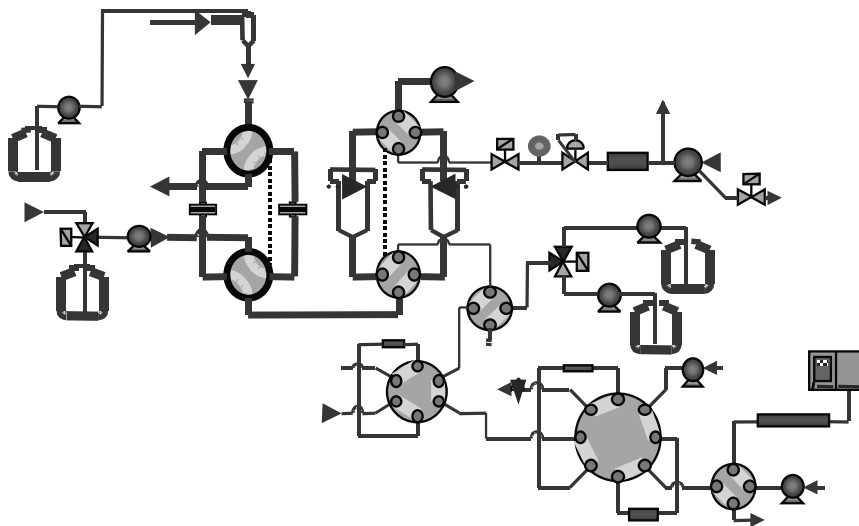
**Figure 2.** Relationship between 2,4,6-TriCP and 1,2,3,7,8-PCDF in flue gas at “C”, Dec. 11 & 12, 2001

CPs in AS were analyzed with three methods. The results of HPLC/ECD were compared with that of HPLC/GC and CD-GC/MS, and some peaks in chromatograms by HPLC/ECD were found to compose practically only one chlorophenol but some include the other compounds. Good correlations are observed among the analytical values of some compounds of CPs by three methods as shown in Fig.1.

*Development of sequential automated monitoring instrument for CPs*

Two types (FGSA-1 and -2) of the sequential automated monitoring instrument were developed until now. One of them is shown in Fig.3. Both of the instruments are composed of four parts, that is, a cooled sampling unit for flue gas, a periodical introduction unit for AS into HPLC, an HPLC with ECD for separation and detection of CPs, and a control unit for each unit and data handling. A removal device (F-1 & F-2 in Fig.3) for dust in AS sample and the collection tube (ODS cartridge, in Fig.3) was newly installed in FGSA-2.

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**Figure 3.** Flow diagram of the instrument (FGSA-2)

The sampling unit has two parallel cooled traps (S-1&S-2 in Fig.3) for continual sampling and the sampling flow rate was adjusted to 2L/min with a mass flow controller in two systems. The sample volume introduced into HPLC was 0.5mL (FGSA-1) and 15-25mL (FGSA-2).

### *Field use of sequential automated monitoring instrument at the waste incinerators*

The developed instruments were tested at three kinds of incinerators, that is, "A" for industrial waste (treatment capability: 70 ton/24 hours) for 10 days, "B" for medical waste (1.2 ton/8 hours) for ten days, and "C" for municipal waste (50ton/16 hours) for 100days. Five compounds of CPs were constantly detected at the level of 1-10,000 ng/Nm<sup>3</sup> and their levels tended to decrease with the much capability. Some of data on CPs were compared with the concentration of PCDDs/-Fs. Certain relationship between some pairs of CPs and PCDDs/-Fs are observed. A good example in 2,4,6-TriCP and 1,2,3,7,8-PCDD shows in Fig. 2.

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