Quantification and Profiling of PCDDs/PCDFs in Stack Gas of Municipal Waste Incinerator on Capillary Column

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Introduction

Since Olie et al.(Netherlands) first detected the polychlorinated dibenzo-p-dioxins and dibenzo furans (PCDDs/PCDFs) emissions from municipal solid waste incinerator (MSWI) in 1977, incinerator facility among the inventories of PCDDs/PCDFs has become the biggest target for interest and been reported as the major contributors of PCDDs/PCDFs to the environment, everywhere.

PCDDs/PCDFs formation mechanism in incinerator has been reported : formation from precursors that have similar to the structure of PCDDs/PCDFs, formation from PCDDs/PCDFs that already exist in waste and de novo formation from high temperature synthesis reaction[1]. These compounds are high toxic persistent organic pollutants that are easily accumulated in organisms as well as body, and very stable to chemical and biological degradation.

Generally, PCDDs/PCDFs analysis from incinerators needs isomer specific analysis that isolate toxic seventeen 2,3,7,8-substitute PCDDs/PCDFs from the other PCDDs/PCDFs and interferences. So seventeen 2,3,7,8-substitute PCDDs/PCDFs should be isolated from various isomers through GC column, otherwise those cannot be effectively analyzed at mass spectrometry.

In this study, the difference of quantification and congeners profiling of PCDDs/PCDFs from incinerator according to the using different GC columns such as SP-2331(polar column) and DB-5MS(nonpolar column) was investigated.

Materials & Methods

Stack gas of MWI(municipal waste incinerator) that was located in Busan city, South Korea was collected using stack sampler (CAE Ltd, USA) equipped with glass filter(Advantec, Japan) and XAD-2 resin(Supelco, USA) according to the Korean standard Method[2]. Collection of stack gas was carried out three times. Internal standard for sampling(37Cl-2378-TCDD, Wellington lab Inc., USA) was spiked into XAD-2 resin prior to sampling. Samples were extracted using a soxhlet extraction and a liquid-liquid extraction with toluene.

To cleanup sample extracts, multi-silica column, alumina column and carbon column were used. Multi-silica column was packed from bottom to top with : 2% KOH-silica gel, 44% H_2SO_4-silica gel, 22% H_2SO_4-silica gel and 10% $AgNO_3$-silica gel. Basic alumina activated by heating in muffle furnace at 600℃ for 24 hours was used for alumina column cleanup. Both columns were tapped to settle the adsorbents. And carbon column was made of 18% w/w mixture of carbopak C and celite 545AW and activated at 130℃ for 6 hours. Cleanup standard(Wellington Ltd, USA) was added to sample extracts prior to sample cleanup.

The instrument analysis of PCDDs/PCDFs was performed by selected ion recording(SIR) and EI positive mode using a AutospecUltima(Micromass Ltd, UK) equipped with HP 6890 series plus gas chromatograph(Agilent, USA). HRGC/HRMS measurement was carried out over 10,000 resolution at 10% valley. For the separation of PCDDs/PCDFs congeners, SP-2331 column(60m×0.32mm×0.2 film thickness) and DB-5MS(60m×0.25mm×0.25 film thickness) were used, respectively. Quantification of PCDDs/PCDFs was performed by an isotope dilution method, using RRF(relative response factor) obtained from 5 calibration standard(Wellington Lab Inc., USA)[3,4].

Results and Discussion

The differences of quantification and congeners profiling of PCDDs/PCDFs emission from municipal solid waste incinerator according to the using different GC columns such as SP-2331(polar column) and DB-5MS(non-polar column) were shown in Table 1, Fig. 1 and Fig. 2. In the case of total amount(non-TEF) of detected dioxin congeners from incinerator, the quantification by SP-2331 column was higher than that by DB-5MS column, especially PCDFs by 30%. The concentrations of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 1,2,3,7,8,9-HxCDF by SP-2331 column were above double on using DB-5MS column. On the other hand, the quantification of 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,6,7,8-HpCDD by DB-5MS column was higher than that by SP-2331 column. Consequently, total amount(non-TEF) by SP-2331 column was 217pg/Nm^3 and higher than that by DB-5MS by 7.3%.

The application of I-TEF to detected dioxin congeners was shown in Fig. 2. PCDFs concentration by SP-2331 column was higher than that by DB-5MS column by 16.4%. On the other hand, PCDDsconcentraton by SP-2331 column was lower than that by DB-5MS column by 45.5%. Consequently, total concentration by SP2331 column was 11.7 pg I-TEQ/Nm^3 and lower than that by DB-5MS column by 7.7%. This result was just opposite to the tendency of total amount(non-TEF) of previous results.

Consequently, in the case of total amount(non-TEF), the quantification by SP-2331 column was higher than that by DB-5MS column, while in the case of application of I-TEF, the result was the reverse. Therefore it could be known that the quantification and congeners profiling by SP-2331 column was different from that by DB-5MS column. It was also reported that polar column such as SP-2331 was effective for determination of PCDDs/PCDFs in environmental samples, fly ash, air, etc, while non-polar column such as DB-5MS was effective for the determination of PCDDs/PCDFs in human samples[5].

Reference

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Table 1. The quantification of 17 dioxin congeners by SP2331 and DB-5MS column.

These values were real concentration, not I-TEQ values.

(pg/Nm^3)

	SP-2331 (Polar column)	DB-5 MS (non polar column)
2,3,7,8-TCDF	7.7 ~ 12.6 (9.8)	0.0 ~ 7.3 (3.8)
1,2,3,7,8-PeCDF	6.0 ~ 10.3 (8.1)	0.0 ~ 5.7 (3.2)
2,3,4,7,8-PeCDF	4.7 ~ 9.3 (6.7)	4.3 ~ 11.0 (7.2)
1,2,3,4,7,8-HxCDF	5.0 ~ 9.3 (7.0)	4.3 ~ 7.0 (5.6)
1,2,3,6,7,8-HxCDF	4.3 ~ 8.0 (5.7)	2.3 ~ 6.7 (4.1)
2,3,4,6,7,8-HxCDF	4.0 ~ 10.7 (6.8)	4.0 ~ 9.3 (6.0)
1,2,3,7,8,9-HxCDF	2.3 ~ 4.3 (3.1)	0.0 ~ 2.7 (0.9)
1,2,3,4,6,7,8-HpCDF	8.7 ~ 18.6 (12.1)	8.0 ~ 21.3 (13.7)

1,2,3,4,7,8,9-HpCDF	0.0 ~ 4.0 (2.3)	0.0 ~ 2.3 (1.3)
OCDF	7.7 ~ 11.0 (9.2)	2.3 ~ 5.3 (3.7)
2,3,7,8-TCDD	0.0 (0.0)	0.0 (0.0)
1,2,3,7,8-PeCDD	0.0 (0.0)	0.0 ~ 11.3 (5.2)
1,2,3,4,7,8-HxCDD	3.3 ~ 14.7 (8.5)	2.3 ~ 13.0 (7.1)
1,2,3,6,7,8-HxCDD	5.0 ~ 30.0 (17.2)	3.7 ~ 27.0 (15.7)
1,2,3,7,8,9-HxCDD	5.7 ~ 21.3 (12.9)	3.0 ~ 17.3 (9.8)
1,2,3,4,6,7,8-HpCDD	19.3 ~ 119.5 (63.2)	20.3 ~ 132.9 (69.8)
OCDD	19.0 ~ 80.3 (44.4)	12.3 ~ 87.2 (44.2)

( ) : average value

Figure 1 Dioxin Profiling of Real Values Figure 2. Dioxin Profiling of I-TEQ Values