Rapid PCDD/PCDF Screening Method for Fly Ash with Ion Trap MS/MS

YUKIO KEMMOCHI*, AND AKIHIRO ARIKAWA
Environmental R&D Dept., EBARA CORPORATION. 4-2-1 Honfujisawa, Fujisawa 251-8502, Japan

*:To whom correspondence should be addressed; fax:+81-(0)466-82-2859;
e-mail:kemmochil0043@erc.ebara.co.jp

Introduction.

Various types of clean-up procedures are used to analyze polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) in environmental samples[1]. The extracts from the environmental samples are placed into the clean-up step so as to remove the matrices which interfere GC/MS analysis. This step is essential for conventional "single mode-of-the-operation" mass spectrometry because these interfering compounds may cause misleading results[2]. However, the clean-up step is one of bottlenecks in the dioxin analysis since it is time-consuming. This is the reason why many researchers are still trying to improve the existing clean-up procedures[3-4] to refine the PCDD/PCDF analysis.

Tandem mass spectrometry (MS/MS) produces the characteristic ions by the secondary ionization. Along with the gas chromatography, the MS/MS presents highly reliable information which helps identification of the compounds[5]. Conventional MS/MS consists of two quadrupole rod assemblies, one for parent ion and another for daughter ion. This instrumentation has many drawbacks; expensive to purchase, hard to maintain, requires a large laboratory space, and labor intensive[6]. However, the recent improvement of the ion trap mass spectrometer eliminates these obstacles[7].

The aim of this study is to optimize the ion trap MS/MS conditions in order to improve the efficiency of the PCDD/PCDF analysis. The optimized MS/MS conditions make it possible to reduce the clean-up procedures because the MS/MS itself is highly selective so that it can be regarded as a part of the clean-up. Fly ash samples were analyzed by this "screening method" with the ion trap MS/MS and the minimized clean-up step, and the results were compared with those obtained by the conventional PCDD/PCDF analytical method.

Materials and Methods.

Screening Method. Sample extraction was performed on a Dionex (Salt Lake City, UT) ASE-200 system. Air-dried samples were mixed with Na_2SO_4 anhydrous and ground using a C.T.C (Tokyo, Japan) TI-100 grinder before the extraction. The extraction was performed at 2000 psi / 170 °C with toluene. Each sample was extracted twice to increase the recovery rate. The extraction took, in total, 55 minutes per one sample. The extract was evaporated to approximately 1 mL, then the sample extract was transferred onto a Supelco (Bellefonte, PA) LC-Si silica gel column (500 mg)

and extracted with 5mL of toluene. The sample was evaporated again to approximately 500 μL, then transferred to a vial and concentrated to 100 μL under N_2. A 30 m × 0.25 mm i.d. Supelco MDN-12 column was used to separate the PCDD/PCDF isomers. A ThermoQuest (Austin, TX) TRACE GC 2000 gas chromatograph equipped with the model AS 2000 autosampler was used for the PCDD/PCDF determination. The oven was held at 100 °C for 1 minute, temperature programmed at 30 °C / min. to 250 °C, held at 250 °C for 17 min., then temperature programmed at 5 °C / min. to 310 °C, held at 310 °C for 5 min. A portion of 1.0-2.0 μL of a standard solution or a sample was injected in to a split/splitless injector. The injector temperature was held at 280 °C. Ion trap MS/MS was performed on a ThermoQuest GCQ plus ion trap mass spectrometer. The ion volume temperature was kept at 200 °C. Both of the precursor isolation time and the excitation time were set for 30 ms. The excitation voltage for tetra to octa chlorinated dibenzo-*p*-dioxins was 1.5 V, for tetra to hexa chlorinated dibenzofurans was 1.8 V and for hepta to octa chlorinated dibenzofurans was 1.9 V. The q value was settled at 0.45. The other MS/MS conditions like the parent ion or segment times are shown in Table 1. On the other hand, conventional analysis were carried out using high resolution mass spectrometry (HRMS)[8].

Table 1. MS/MS Conditions

compound	time	parent ion range (*m*/*z*)	daughter ion range (*m*/*z*)	quan. ion (*m*/*z*)
T4CDD	12.0 - 16.9	319.9 - 323.9	257 - 259	257 + 259
P5CDD	17.0 - 24.4	353.9 - 357.9	291 - 293	291 + 293
H6CDD	24.5 - 30.9	387.8 - 393.8	325 - 327	325 + 327
H7CDD	31.0 - 33.9	421.8 - 427.8	361 - 363	361 + 363
O8CDD	34.0 - 40.0	455.7 - 463.7	395 - 397	395 + 397
T4CDF	11.7 - 15.4	303.9 - 307.9	241 - 243	241 + 243
P5CDF	15.5 - 22.9	337.9 - 341.9	275 - 277	275 + 277
H6CDF	23.0 - 30.4	371.8 - 377.8	309 - 311	309 + 311
H7CDF	30.5 - 34.2	405.8 - 411.8	345 - 347	345 + 347
O8CDF	34.3 - 40.0	439.7 - 447.7	379 - 381	379 + 381

Standards and Samples. A Cambridge Isotope Laboratory (Andover, MA) EDF-4067 certified stock solution containing 17 tetra to octa PCDD/PCDF ($^{13}C_{12}$, 99%) (2,3,7,8 isomers) in nonane was diluted with toluene to appropriate levels for the analysis and used as internal standards. EDF-9999 certified calibration solution was used for calibration. The fly ash samples were received from municipal solid waste incinerator. The quantitation ions of the ion trap MS/MS are shown in Table 1.

Results and Discussion

The screening method using ion trap MS/MS and the conventional analysis with the HRMS both led practically the same results as shown in Table 2. The TEQ values obtained by the screening

method tend to be slightly higher than those obtained by the conventional method.

The differences of the TEQ between the two methods can be explained by their analytical procedures. In the screening method, the internal standards were added just before the extraction. On the other hand, the internal standards were added after the extraction in the conventional analysis (see Figure 1). Obviously, the sample losses during the HCl Treatment, Soxhlet Extraction or Liquid-Liquid Partitioning in the conventional analysis had caused the differences. The screening method is very simple and the coincidence to lose the PCDD/PCDF in the clean-up step is rather low compare to the conventional analysis. The average of the recovery of the 17 internal standards in the ion trap MS/MS analysis was excellent (105% , CV=12%) due to its simplicity.

Table 2. The Comparison between Conventional Method and Ion Trap MS/MS (n=4)

2,3,7,8 isomers	conventional method	ion trap MS/MS		ratio (average)
	TEQ [pg/g]	TEQ [pg/g]	conc. [ng/g]	
2378-T4CDD	3.1	n.d.	< 0.01	N/A
12378-P5CDD	16	22	0.04	1.5
123478-H6CDD	7.9	11	0.11	1.4
123678-H6CDD	33	45	0.45	1.4
123789-H6CDD	18	23	0.23	1.3
1234678-H7CDD	46	57	5.7	1.2
O8CDD	18	19	19.0	1.1
2378-T4CDF	2.1	8	0.08	3.8
12378-P5CDF	10	11	0.22	1.1
23478-P5CDF	100	126	0.25	1.3
123478-H6CDF	50	56	0.56	1.1
123678-H6CDF	78	92	0.92	1.2
123789-H6CDF	110	168	1.7	1.5
234678-H6CDF	15	23	0.23	1.5
1234678-H7CDF	52	70	7.0	1.3
1234789-H7CDF	17	18	1.8	1.1
O8CDF	8.9	10	9.9	1.1
Total TEQ	585	758	-	-
average	-	-	-	1.3
C. of V.	-	-	-	12 %*

*:2378-T4CDD and 23478-P5CDF are excluded.

The major drawback of the screening method is the method detection limit (MDL). The instrumentation of the ion trap MS/MS can identify as small as 0.5 pg of 2,3,7,8-T4CDD standard. However, the actual detection limit is 10 times as high because the interfering compounds in the fly ash made the signal-to-noise ratio worse. In this study, 10-20 g of fly ash was used for one

analysis. So, the MDL of the ion trap MS/MS analysis was about 12.5 pg/g at lowest per each isomer. This is the reason why 2,3,7,8-T4CDD could not be analyzed by the screening method. Nevertheless, this MDL did not affect the TEQ results much as the contribution of the 2,3,7,8-T4CDD is small compared to the other 2,3,7,8-isomers. There is no rational explanation to clarify the differences of the 2,3,7,8-T4CDF quantitation so far.

Even though this fairly high MDL is taken into the account, the screening method with the ion trap MS/MS is a considerably practical method for the PCDD/PCDF analysis.

References

1) Finkel, J. M., James, R. H., Baughman, K. W. *Chemosphere,* **1989,** *19,* 67-74
2) Samsonov, D.P., Evdokimov, K. Y., Zhiryukhina, N. P., Kiryukhin, V. P., *J. of Anal. Chem.,* **1998,** *53,* 754-758
3) Hays, M. J., Riggs, K. B., *Organohalogen Compounds,* **1995,** *23,* 113-117
4) Höckel, J., Düsterhöft, L., Körner, W., Hagenmaier, H., *Organohalogen Compounds,* **1995,** *.23,* 135-138
5) Karasek, F. W., Clement, R. E., *Basic Gas Chromatography-Mass Spectrometry: Principles and Techniques,* Amsterdam: Elsevier Sciense, **1988**
6) Plomly, J. B., Mercer, R.S., March, R. E., *Organohalogen Compounds,* **1995,** *23,* 7-12
7) Leonards, P. E. G., Brinkman, U. A. Th., Cofino, W. P., *Chemosphere,* **1996,** *32,* 2381-2387
8) Takasuga, T., Inoue, T., Ohi, E., *J. of Environ. Chemistry,* **1992,** *2,* 599-613
9) van Bavel, B., Takeda, N., Inoue, T., Ishihara, S., Ito, H., Kohno, S., Miyata, H., Morita, M., Sandell, E., Takasuga, T., Rappe, C., *Organohalogen Compounds,* **1994,** *19,* 265-268