

The development and certification of Ash CRM for PCDD/Fs

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Introduction

Certified Reference Material (CRM) is needed for checking a test method or for investigating the quality of analysis of a laboratory or company. Because Municipal waste incineration is one of the main PCDD/Fs emission sources, many researchers have studied to reduce the emission of PCDD/Fs from a incinerator. In order to confirm the effect of new technology on reducing PCDD/Fs release from incinerator, a number of test of PCDD/Fs in various samples are required. Especially, ash sample as well as exhaust gas from incinerator is analyzed for showing the PCDD/Fs reduction efficiency of new technology installed on the incinerator. However, because it is not easy to find a proper Ash CRM for PCDD/Fs in Korea, the CRM is needed to develop.

Materials and methods

1. Collecting sample

About 40 kg ash samples were collected from the Electro static Precipitator (EP) of a municipal waste incinerator at thirty-minute interval for eight hours. The amount of sample was reduced to be about 10 kg on the basis of official Korean test method for waste. Sample was put in an amber glass bottle and transferred to the laboratory.

2. Homogenizing sample

Homogenizing sample is an important step among several procedures of developing an Ash CRM. Sample was dried at 100 °C in a drying oven. Large size particles in sample were removed with analyst's own hands. And then sample was homogenized by using a homogenizer for 4 hours. Homogenized sample was screened out with a 75µm mesh sieve. A part of sample remaining on top of the sieve was again homogenized with a homogenizer for 4 hours and tried to sieve again with the 75µm mesh sieve. This full homogenizing step was performed twice repeatedly. After homogenization step, sample was divided into 90 sample bottles. Sample weight in each bottle is about 10g. The bottles were tightly stopped.

3. Analysis for PCDD/Fs

EPA method 1613 was used for analyzing PCDD/Fs. Samples were extracted with a soxhlet apparatus. Toluene

was used as the extraction solvent. The extracts were pretreated with a multi-layer silica gel clean up, Alumina clean up and activated carbon clean up procedures. A HRGC/HRMS (Autospec Ultima, Micromass co. U.K) was used to analyze PCDD/Fs. A SP-2331 capillary column of 60m length and 0.32 mm internal diameter with a 0.20 um film thickness was used in analysis. All standards used in this study were manufactured at Wellington Co

Result and discussion

1. Evaluation of distribution of particle size in CRM

To evaluate sample particle size, we selected randomly three sample bottles among 90 sample bottles. The results are showed at Figure 1. About 89% of particle sizes in all samples were less than 75um mesh size.

2. Evaluation of between-bottle homogeneity in CRM

To evaluate between-bottle homogeneity in CRM, we selected randomly five sample bottles and analyzed PCDD/Fs in them. The KESS program was used to obtain mean and standard deviation. The average of PCDD/Fs concentration in five sample bottles was 30.357 ± 4.280 ng I-TEQ/g at the 95% confidence level and the results are shown at table 1.

3. Evaluation of whinin-bottle homogeneity in CRM

To evaluate within bottle homogeneity in CRM, we selected randomly two bottles and made three sub-samples from each of 2 sample bottles. All six sub-samples were analyzed and the results are shown at Table 2. The average of PCDD/Fs concentration in six sub- samples was 30.744 ± 3.033 ng I-TEQ/g at the 95% confidence level.

The distribution statistic result P value of two groups, between–bottle samples and within-bottle samples, is 0.8448. From the result, two groups are proved to be the same.

4. Evaluation of stability of CRM

For the stability test of CRM, we analyzed samples after 7 days and 30 days, respectively. The results were 28.665 ng I-TEQ/g in sample after 7 days and 29.079 ng I-TEQ/g in sample after 30 days. The p value of two groups was 0.2059. From the result, we confirmed stability of samples. However, the study of stability is needed to continue.

5. Evaluation of uncertainty in PCDD/Fs analysis procedure

5-1. Determining uncertainty factor

In PCDD/Fs analysis, several procedures were performed but only three steps, sample divide step, standard spike injection step and instrument analysis step, were considered to be major uncertainty factors in this study.

1) Sample divide step (u(D))

The uncertainty factor of sample divide step was measured at the equation 1. d means dilution intensity of sample and u(f) and u(p) mean uncertainty of volumetric flask and Pipette used in analysis.

$$\frac{u(d)}{d} = \sqrt{\left[\frac{u(p_1)}{p_1}\right]^2 + \left[\frac{u(f_1)}{f_1}\right]^2 + \left[\frac{u(p_2)}{p_2}\right]^2 + \left[\frac{u(f_2)}{f_2}\right]^2} \quad \text{Equation 1.}$$

2) Standard spike step (u(C_I))

In this step, the uncertainty of internal standard concentration used and micropipette used were measured at equation 2. u(C_{IS}) means the uncertainty of internal standard concentration, u(V_{mp}) mean the uncertainty of pipette and u(W) means uncertainty of ability of analyst.

$$\frac{u(C_I)}{C_I} = \sqrt{\left[\frac{u(C_{IS})}{C_{IS}}\right]^2 + \left[\frac{u(V_{mp})}{V_{mp}}\right]^2 + \left[\frac{u(W)}{W}\right]^2} \quad \text{Equation 2.}$$

3) Instrument analysis step (u(GC))

In this step, the uncertainty of internal standard concentration used and calculating of RRF were measured at equation 3. u(C_{VS}) means the uncertainty of calibration standard concentration and u(RRF) means the uncertainty of calculating average RRF

$$\frac{u(GC)}{GC} = \sqrt{\left[\frac{u(C_{VS})}{C_{VS}}\right]^2 + \left[\frac{u(RRF)}{RRF}\right]^2} \quad \text{Equation 3.}$$

5-2. Calculating expanded uncertainty

From the result of three uncertainty factors, expanded uncertainty was calculated at equation 4. Before calculating the expanded uncertainty, the combined standard uncertainty was required to be calculated. A following equation was used to calculate the combined standard uncertainty.

$$\frac{u(C)}{C} = \sqrt{\left[\frac{u(d)}{d}\right]^2 + \left[\frac{u(c_I)}{C_I}\right]^2 + \left[\frac{u(GC)}{GC}\right]^2} \quad \text{Equation 4.}$$

The expanded uncertainty was calculated through multiplying the combined standard uncertainty by confidence coefficient. The result was 30.567±0.958 ng I-TEQ/g (at the 95% confidence level, k=2)

Figure 1. The result of the distribution of particle size in three samples

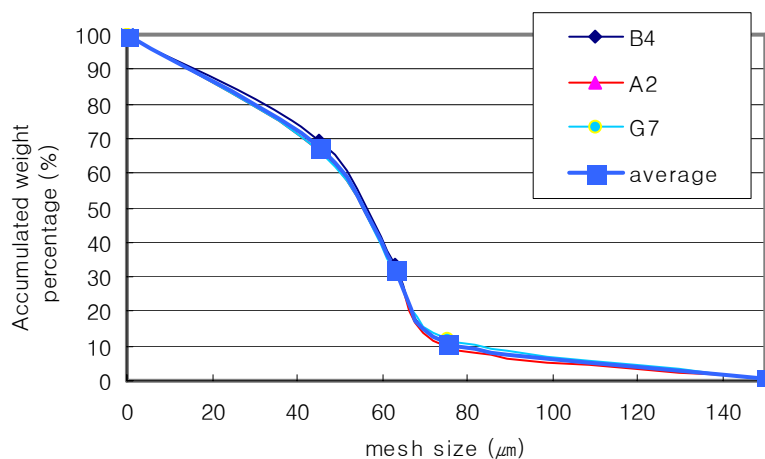


Table 1. The statistic result of between-bottle sample

Content	Data
Mean	30.3566
Median	30.998
Number of sample	5
Standard deviation	3.4476
Standard deviation of the mean	1.5418

Table 2. The statistic result of within-bottle sample

Contents	Data
Mean	30.7422
Median	30.8565
Number of sample	6
Standard deviation	2.8895
Standard deviation of the mean	1.1796

References

1. Preparation and certification of the new reference material fly ash for dioxin analysis(Yoshio Iida, Hiroyuki Igaki etc, Bunseki Kagaku, Vol.50, No.8, pp. 571 ~ 576, 2001)
2. Development and certification of a coal fly ash certified reference material for selected polycyclic aromatic hydrocarbons(Xueli Cao, Xiaobai Xu, Wenxuan Cui, Zhiqun Xi, Fresenius J Anal Chem 370 pp. 1035 ~ 1040, 2001)
3. FLY ASH CRM 490: A new BCR Certified reference material for PCDD/PCDF analysis (R.Van Cleuvenbereen , G.N. Kramer, E.A. Maier, Chemosphere, Vol. 37, Nos 9-12, pp. 2425 ~ 2438, 1998)
4. Evaluation of a new automated cleanup system for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in environmental samples (E. Abad, J. Saulo, J. Caixach, J. Rivera, Journal of Chromatography A, 893 pp. 383 ~ 391, 2000)