MEMORY EFFECT ON PCDD/F SAMPLING BY UTILIZING ADSORPTION METHOD FOR SAMPLING OF DIOXIN (AMESA) IN VARIOUS SOURCES

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Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emission has been considered as a very important pollution issue in many countries of the world since they were found in the flue gas of a municipal solid waste incinerator in 1977.[1] The regulated standards has been established and tightened for various PCDD/F potentially emission sources, such as municipal solid waste incinerator (MSWIs), electrical arc furnace (EAFs), sinter plant and secondary aluminum smelting. The PCDD/F levels in flue gas of the aforementioned industries were regularly checked only twice a year in Taiwan. However, these temporary samplings cannot stand for the annual average emission, for example, an MSWI is reported to emit significantly high concentration of PCDD/Fs, resulted from the incompletely combustion during the start-up process[2]. The PCDD/Fs is more contributed by the casually pulse and short-period emission induced by unstable operation than by the normally continuous emission. Nevertheless, the PCDD/Fs impacts to the environment and human health cannot be controlled in time while the abnormal operation happens and air pollution control devices are broken because the PCDD/F levels cannot be continuously monitored by the current conventional sampling techniques.

For improving the sensitivity of the PCDD/F monitoring system, an Adsorption MEthod for SAmpling (AMESA) of Dioxins and Furans has been developed and utilized in various emission sources in Europe. A series of performance tests has followed the "German Guideline for the Qualification of Continuous Emission Monitoring System (CEMS)", which was notified by European Union, to ensure the long-term sampling process since 1995.[3] The AMESA employed in this study is produced by Environnement S.A Deutschland, which is able to continuously collect the persistence organic pollutants, such like PCDD/Fs and polychlorinated biphenyls (PCBs), in the flue gas. This method has been verified by comparing with EN1948 manual sampling method in WIs and shown very good correlation.[4,5] The R^2 of the linear regression between the PCDD/F I-TEQ concentrations by AMESA and JIS-TYPE I (improved with cool probe) goes up to 0.97, showing a strong relationship.[6] However, the inter-method RSD is reported as 21.9% between AMESA and EPA 23A for the PCDD/F collections during short-term samplings[7]. Nevertheless, the AMESA system is only applied to the waste incinerators today. Therefore, not only the short-term AMESA sampling, but various potential PCDD/F sources should further be tested. In this study, AMESA is compared with the regular manual sampling (MS) method in term of short- and long-period sampling to analyze the correlation between methods used in a sinter plant, an MSWI, and an EAF.

Materials and methods

Two sampling method was utilized to collect the PCDD/Fs from the flue gases. The regular PCDD/F MS method in this study followed EPA Modified Method 23A. For the AMESA sampling, a glass cartridge packed with quartz-wool and XAD-II was installed before an isokinetic sampling pump to collect the particulate and gaseous phase PCDD/Fs, respectively. The most different part between AMESA and MS is that the cool probe ($<50^{o}$C) is used to extract the flue gas isokinetically in AMESA system instead of a heated probe ($>120^{o}$C). After adsorption, the measured gas is pumped through a flexible tube to the control cabinet, where the gas was cooled down to $<5^{o}$C to completely remove the condensate. AMESA operates totally automatically and all necessary data can be recorded and transferred to the computer. After sampling period, the cartridge and stored information are transferred to the laboratory for further analyses of PCDD/Fs.

The experiment design of this study was separated into two parts. The first one was to evaluate the influence of the residual PCDD/F accumulated on the inner surface of AMESA by conducting the real scale PCDD/F

sampling from three specific emission sources, including a sinter plant, an MSWI, and an EAF. A series of five-time washing was taken after 8 long-period sampling. The eluent from each washing process was collected and analyzed for the PCDD/F content to quantify the effect of the residual matter in the AMESA sampling system. All the washing eluents were added into the cartridge and analyzed as an overall PCDD/F concentration of a long-term sample. For the sampling strategy, two AMESA long-period samples (168 hours) were collected after three short-period ones (4-6 hours) in the sinter plant. On the other hand, two groups of two-long-period samples were collected from the flue gases of MSWI and EAF, respectively, before the short ones to build a potentially accumulative condition for comparison. The above arrangement focuses on the change of the PCDD/F level in short-term samples before and after the long-term ones in order to examine if there are memory effect along with the long-term AMESA sampling.

The other part of this study focuses on the suitability of AMESA in a relatively stable operated sinter plant, which has no experiment done around the world. A long-term sampling comparison by AMESA and standard MS were the most ideal proof but cannot be applied, because of the MS sampling time limit is only few hours to maintain the sampling precision. Hence, the 16 parallel (AMESA and MS) tests were taken with the short period in this study. Furthermore, 8 long-period AMESA samples, followed by the other 16 short-period samples, were taken place from a sinter plant (a more steadily operated source) to collect enough information for more statistical calculation, and further analyze the correlation between AMESA and MS. Finally, a conclusion of the suitability of AMESA for the specific stationary sources will be conducted.

Results and discussion

Two-stage cartridge was considered as the major PCDD/F collecting unit in this study. However, the relatively high dioxin and I-TEQ masses found in the second cartridge (< 10 %) were quite unusual for the sampling method in which breakthrough is normally below 1 %. This relatively high breakthrough could be caused by very fine particles in the flue gas of the sinter plant. Therefore further tests will be done with implemented fine dust filter. On the other hand, the PCDD/F residual fraction in AMESA sampling units (probe and flexible tube) were quantified by the eluents collected from the washing processes after 8 long-term AMESA samplings. Figure 1 shows the mass distributions of PCDD/F and I-TEQ in cartridges and washing eluents. The sum of total PCDD/Fs in the above units is defined as a long-term sample. Total PCDD/F and I-TEQ mass in the 1st eluent are equal to 21.8 and 19.7% masses of the first cartridge, respectively, while the total PCDD/F and I-TEQ mass in the 2nd eluent are equal to 0.411 and 0.185% mass of the first cartridge. The above result indicates a significant reduction of PCDD/F I-TEQ mass with the washing time, representing that the residual effect of PCDD/F I-TEQ will be greatly inhibited (lower than 0.2%) after one-time washing.

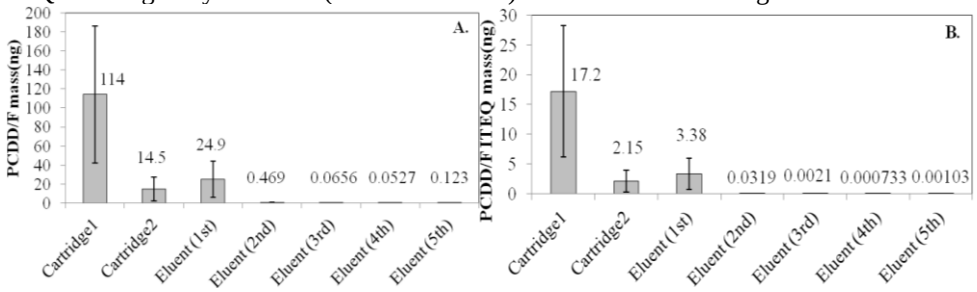

Figure 1 Mass distribution of PCDD/F (A) and I-TEQ (B) in cartridges and washing eluents

For the sinter plant, three short-period samples were taken by AMESA and MS, which were followed by two long-period AMESA samplings (Figure 2). PCDD/F I-TEQ concentrations are 0.25 ng I-TEQ/Nm^3 (n=2, RSD=25.1%) and 0.144 ng I-TEQ/Nm^3 (n=3, RSD=12.9%) by using AMESA and MS, respectively. The relative percent difference (RPD) between these two methods is 41.3%. This indicates the AMESA and MS can provide the similar total PCDD/F I-TEQ information for sinter plant during short-period sampling. For the long-period sampling, AMESA shows 151 and 64.1% higher values than those collected by AMESA and MS in short time. The above result could be due to the more complete collection of PCDD/Fs by a longer period, including several casual unsteady operation and emission within 168 hours. For deeply investigating the memory effect, the congener profiles of three short-period samples were displayed in Figure 2. The OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF dominates the PCDD/F emission collected by AMESA, while PCDFs is the major group by MS. Notably, the fraction of highly chlorinated PCDD/Fs, OCDD, in short-period AMESA samples is obviously higher than that in the MS sample, and decrease with the sapling time from 34.6 to 32.4

and 26.9%. This means AMESA could be affected by the residues, including the particulate matters and condensed gaseous PCDD/Fs at the temperature <50°C in the sampling system.

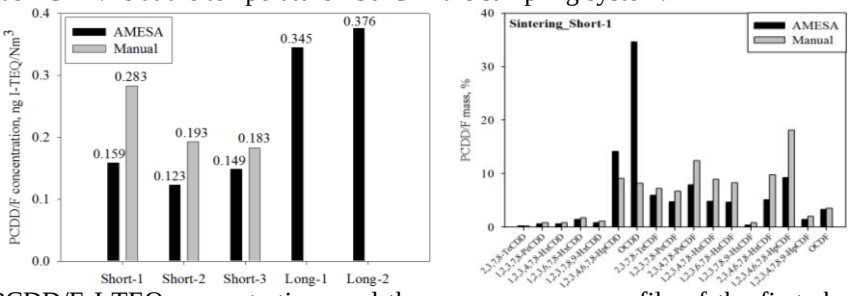

Figure 2 Total PCDD/F I-TEQ concentrations and the congener mass profile of the first short-period sample collected from a sinter pant by AMESA and MS

The sampling strategy of the MSWI is opposite to that of the sinter plant to examine the effect of long-term operation (Figure 3), while all the samples were collected during the start-up operation of the MSWI. Results show that the PCDD/F level in the first long-term sample is 2.2 times (0.457/0.208) to the second one, indicating the relatively higher emission during the start-up process and further decreases with time. Interestingly, the PCDD/F I-TEQ level of the first short-period AMESA sample is dramatically higher than the previous long-period AMESA samples, and it does not follow the normal PCDD/F decreasing trend after the MSWI start-up.[8] This phenomenon provides a sign of the PCDD/F memory effect in the AMESA system as it was investigated already in earlier tests[9]. Therefore the AMESA system is generally provided with a changeable inner tube for an easier probe cleaning if necessary. For the congener mass profile analysis, the dominant OCDD and 1,2,3,4,6,7,8-HpCDD in the congener profiles of the 1st short-period sample supports the above inference. Later on, the accumulated OCDD fraction sharply decreases with time and washing treatments from 1.25 to 0.415 and 0.177, which is close to the MS level.

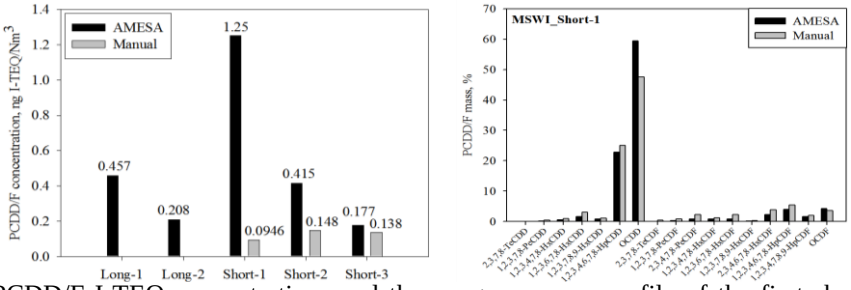

Figure 3 Total PCDD/F I-TEQ concentrations and the congener mass profile of the first short-period sample collected from a MSWI by AMESA and MS

For the PCDD/F emission from EAF, the long-term AMESA sampling from EAF can provides similar PCDD/F I-TEQ information to those of regular MS samplings when there was no special operation, such as start-up case in MSWI (Figure 4). However, in short-term samplings, AMESA samples show very significant higher PCDD/F I-TEQ concentrations than MS samples. This is due to the release of surface accumulated PCDD/Fs in AMESA system after long-time operation. From MS sample, we can see that the PCDD/F congeners are dominated by lowly chlorinated PCDFs, and the fraction of OCDD and 1,2,3,4,6,7,8-HpCDD are greatly lower than those in MSWI. Thus, the accumulation effect of OCDD is not obvious, and the OCDD fraction provided by AMESA is lower than that of MS sample even the short-term AMESA samplings took place after the long-term AMESA samplings. However, the accumulated lowly chlorinated PCDFs, which have greater I-TEF, in AMESA samples result in much higher I-TEQ concentrations, compared to those of MS samples due to the long-term AMESA samplings.

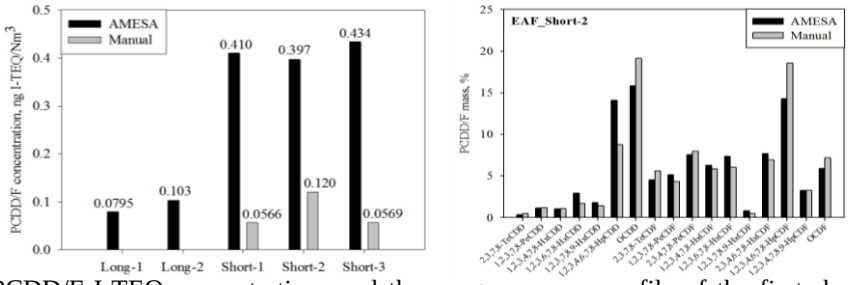

Figure 4 Total PCDD/F I-TEQ concentrations and the congener mass profile of the first short-period sample collected from an EAF by AMESA and MS

After three real case studies, the memory effect to the PCDD/F I-TEQ levels in short-term samples after long time AMESA operation might not be ignored. This conflicting result to the aforementioned one-time washing has to be discussed. The absolute PCDD/F and I-TEQ mass of the 2nd eluent may be ineffective to the long-term AMESA sampling, but it became the interference in the short-term samples. Table 1 shows the comparison between the PCDD/F residues in the 2nd eluent and three short-term AMESA samples. Obviously, the PCDD/F and their I-TEQ masses in the eluent are equal up to 51.4 and 37.0% of the short-term samples. These high ratios will definitely increase the PCDD/F and I-TEQ in following short-term samples. Therefore, the memory effect of the system residues cannot be ignored, especially when AMESA is used for the short-period sampling.

Table1 Residual effect of sampling system after two-time washing on short time sampling

Mass (ng)	Short-1	Short-2	Short-3	3rd eluent (residual)	Residual effect (%)
PCDD/Fs	1.492	2.770	0.913	0.469	16.9-51.4%
PCDD/F I-TEQ	0.171	0.186	0.0862	0.0319	17.2-37.0%

For the suitability analysis of AMESA in sinter plant, there were 8 long-term AMESA samples collected and followed by 32 short-term samples taken by each AMESA and MS for the statistical calculation in this study. Pearson correlation was utilized to describe the relationship between these two sampling methods on 32 samples. In Table 2, the correlation derived by raw 32 PCDD/F and I-TEQ concentrations, provided by AMESA and MS, are not significant at *p*-values equal to 0.476 and 0.864 (>>0.05), respectively. Additionally, their *r*-values also point out a not significant linear correlation between AMESA and MS data. This is resulted from the sampling strategy that previous 8 long-term AMESA sampling might produce obvious memory effect for the later short-term ones. The first three short-term samples are found to have the extremely higher OCDD content, which is caused by the memory effect, and also have much higher PCDD/F I-TEQ levels. Thus, these three data are excluded from the Pearson correlation calculation and derive new parameters (n=29). For the data excluded from the memory effect, *p*-value (0.001) show a significant correlation between the PCDD/F I-TEQ concentrations conducted from AMESA and MS, as well as a more linear correlation at *r*-value equal to 0.597. Consequently, AMESA can provide reliable PCDD/F data with a function of those taken by manual sampling when there is no significant memory effect. AMESA is suggested to be utilized as a long-term PCDD/F sampling method in order to dilute the memory effect and also collect more comprehensive condition of the flue gas that cannot be monitored by the traditional manual sampling.

Table 2 Pearson correlation of AMESA and manual sampling data

Statistical parameters	Total PCDD/Fs concentration		Total PCDD/F I-TEQ concentration	
	Raw (n=32)	Excluded from the memory effect (n=29)	Raw (n=32)	Excluded from the memory effect (n=29)
r-value	-0.131	0.580	-0.0315	0.597
p-value	0.476	0.001	0.864	0.001

Marked correlations are significant at p < .05000

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