Development of a continuous sampling system for POPs measurement

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Introduction

Concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) emitted from municipal wastes incinerators (MWIs) vary significantly with waste component, combustion condition, operating stages and air pollution control devices equipped. Traditional manual sampling method is difficult to accurately measure the POPs emitted during unstable operating stage of MWI. Therefore, developing of automatic continuous stack emission monitoring systems is important for solving these problems. Three types of continuous sampling (filter/cooler method, dilution method, cooled probe method) systems are available for stationary sources followed European committee for standardization (CEN EN-1948). However, the systems developed so far are bulky and difficult to move during sampling and auditing process. Besides, the methods of dilution and cooled probe are significantly different from Taiwan EPA NIEA A807.75C. In order to meet the regulations of NIEA A807.75C, developing a continuous sampling system which is compact and reliable for stack sampling is an important task.

Previous studies indicate that PCDD/Fs will not penetrate through the sampling system if the inlet adsorbent temperature is <50^{o}C (Mayer et al., 2000; Reinmann, 2014). Kahr (2004) indicated that the adsorption efficiency of PCDD/Fs achieves 100% as the inlet adsorbent temperature is controlled at 40^{o}C and >95% at the temperature of 60^{o}C. Besides, both the amount and species of adsorbent used have significant impact on sampling efficiency. Thus, the continuous stack emission monitoring system developed is tested for the sampling efficiencies of PCDD/Fs emitted from an MWI based on three parameters (XAD-2 amount, inlet temperature of XAD-2 and adsorbent species) for 10 days. Additionally, comparison between the continuous emission monitoring system developed and manual sampling method followed NIEA A807.75C in short-term sampling of PCDD/Fs is made in this study.

Materials and methods

National Central University continuous stack sampling system (NCU-CS^3) (as shown in Figure 1) developed in this study has the advantages of small size (1240*660*495 mm), high mobility and low power consumption (<1300W). NCU-CS^3 consists of a heated glass sampling tube, filter, adsorbent (XAD-2) and control system. Both filter and XAD-2 sorbent are spiked with isotopically labeled surrogate standards. The flue gas was withdrawn isokinetically from the stack and passed through the filter and XAD-2 to capture solid-phase and gas-phase pollutants, respectively. The control system is composed of the gas composition analysis system (O_2 and CO_2), isokinetic suction system that controls the gas flow rate (8-10 lpm), pressure and temperature and moisture collection system. The filter, XAD-2 and rinse of the sampling tube are pretreated and analyzed on the basis of Taiwan NIEA A808.75B. These samples were extracted by Soxhlet method, concentrated and analyzed by HRGC/HRMS (for 17 PCDD/Fs and 12 PCBs) and HRGC/MS/MS (for 4-8Cl PCN, 24 PAH, 3-5Cl chlorinated phenols, CPs, 3-6Cl chlorinated benzenes, CBs) with isotope dilution method. Penetration of PCDD/Fs through the NCU-CS^3 is evaluated by installing two adsorption tubes in series and is calculated as the ratio of PCDD/Fs TEQ concentration in secondary adsorption tube and the total PCDD/Fs TEQ concentration (rinse+ filter +first and secondary adsorption tube) (Eq1). The operating parameters are controlled as followed: XAD-2 amount of the 1^{st} adsorption tube is 35, 70 or 100 g (secondary XAD-2 tube is controlled at 70 g); inlet adsorption temperature is between 10-50^{o}C and types of adsorbent applied (XAD-2 or XAD-4).

$$\text{Penetration (\%)} = \frac{\text{PCDD/Fs TEQ concnetration in secondary XAD−2}}{\text{total TEQ concentartion}} \times 100\% \quad \text{(Eq1)}$$

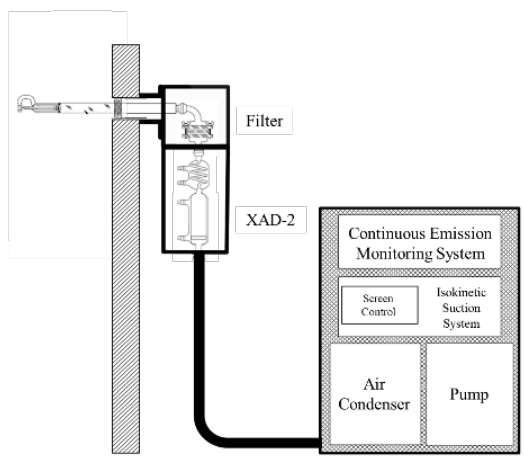

Figure 1. Schematic of NCU-CS^3 developed for continuous sampling of POPs

Results and discussion

The difference between manual sampling and NCU-CS^3 in collecting PCDD/Fs from gas stream is evaluated via short-term stack sampling (6-7.3 hr) of an MWI. The results indicate that relative standard deviations (RSD) of PCDD/Fs concentration between manual sampling and NCU-CS^3 are < 20%, and high correlation coefficient (R^2=0.93) is found in this sampling campaign. It suggests that NCU-CS^3 is reliable and can overcome the disadvantages of manual sampling method (NIEA A808.75B).

The effects of XAD-2 amount and inlet temperature of XAD-2 on the penetration of PCDD/Fs through NCU-CS^3 are shown in Figure 2. The results indicate that penetration increases with increasing inlet temperature of XAD-2 and decreases with increasing XAD-2 amount. Except for the case of 35 g XAD-2, the penetrations are all <1% as the inlet XAD-2 temperature is controlled < 20^{o}C. It implies that 70 g of XAD-2 is optimal in NCU-CS^3 for ensuring effective capture of PCDD/Fs. Furthermore, the results indicate that the penetration of low chlorinated congeners (TCDD/Fs and PeCDD/Fs) is significantly higher than that of highly chlorinated congeners (HxCDD/Fs, HeCDD/Fs, and OCDD/Fs) due to higher vapor pressures.

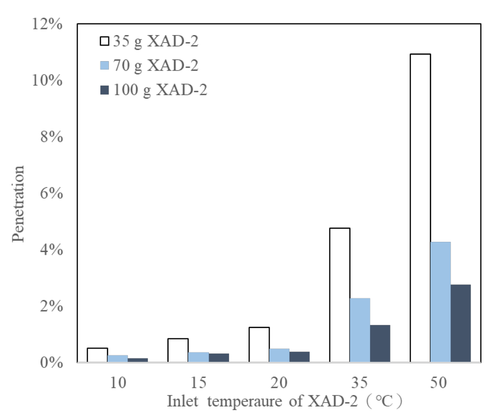

Figure 2. Effects of XAD-2 amount and inlet temperature of XAD-2 on the penetration of PCDD/Fs in NCU-CS^3

According to the aforementioned results (Figure 2), penetrations of PCDD/Fs in NCU-CS^3 are lower than 5% except for 35 g XAD-2 operated at 50^{o}C. Penetration of different POPs are also evaluated simultaneously as shown in Figure 3. The results indicate that penetration of 12 dioxin-like polychlorinated biphenyls (PCBs) is slightly higher than that of 17 PCDD/Fs due to higher vapor pressures of PCBs in comparison to PCDD/Fs. In addition, co-planar PCBs which have higher adsorption potential, exhibiting lower penetration than non-planar PCBs. Polychlorinated naphthalenes (PCNs) have higher vapor pressure, resulting in higher penetration in comparison with PCDD/Fs. Furthermore, higher vapor pressures of polycyclic aromatic hydrocarbons (PAHs), CBs and CPs result in higher penetration in comparison with PCDD/Fs. Especially, penetration of 2-3 rings PAHs are even higher than 20%. It indicates that the structure and the vapor pressure of the compounds to be sampled have significant effects on the penetration of POPs as NCU-CS^3 is applied.

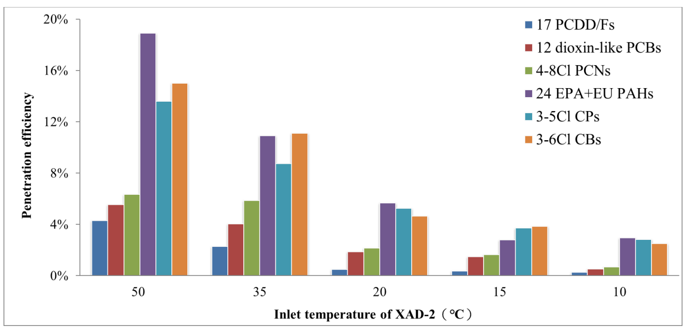

Figure 3. Effects of inlet XAD-2 temperature on penetration of POPs

Since the penetration of PAHs, CPs and CBs are high with XAD-2 as adsorbent, XAD-4 is used as alternative adsorbent to test the penetration. The result indicates that the penetrations of POPs with XAD-4 as adsorbent are lower than that with XAD-2. It is attributed to its higher specific surface area (750 m^2/g) and higher pore volume (0.98 mL/g) compared with XAD-2 (300 m^2/g of specific surface area and 0.65 mL/g of pore size). In conclusion, NCU-CS^3 is a reliable continuous stack gas sampling system for POPs measurement in MWI and the effects of amount and operating temperature of adsorbent on POPs penetration have been evaluated in this study.

Acknowledgements

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