Development of Standard Gas Generation Equipment for Dioxins and Related Compounds in Wide Concentration Range

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Introduction

We have to collect flue gas in actual facilities or atmospheric air for development and evaluation of retardation and monitoring techniques of dioxins and related compounds. However, there are many problems such as instability of concentration and coexisting substances, and restriction of place and time in the field.

We developed a standard gas generation equipment that is able to generate safety dioxins and related compounds such as chlorophenols and chlorobenzenes in low and extremely wide concentration range from 10^{-12} g/m^3 to 10^{-1} g/m^3. Also, in order to predict the generating concentration, we proposed an estimation method of vapor pressure of dioxins and related compounds.

Design of Standard Gas Generation Equipment

Figure 1 shows schematic of the generation equipment. It is necessary for the equipment to be safety enough, and to generate gas stably in wide concentration range.

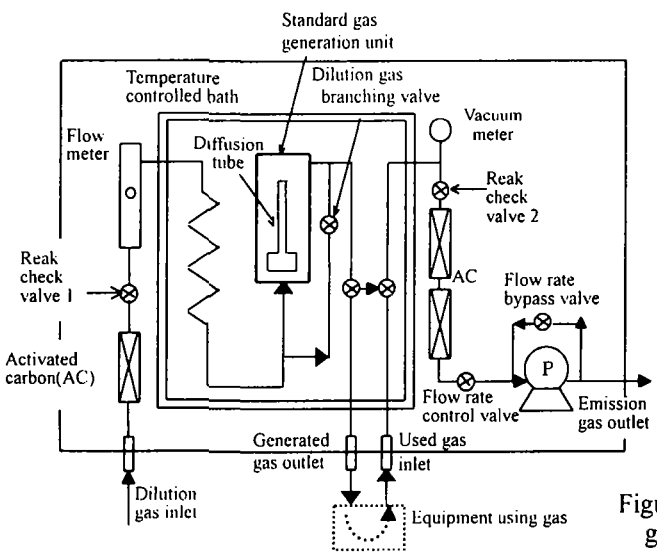

Figure 1 Schematic of developed gas generation equipment

Therefore, a function for monitoring leakage, a warning buzzer for prevention mis-operation, a function for cleanup of the pipe in the equipment were installed. The generated gas return to the equipment after use and is introduced to two columns in which activated carbon was packed sufficiently. Furthermore, the inside of the equipment was made negative pressure with paying attention to safety measures. The equipment in which diffusion tube is used and the dilution gas can be branched for stable generation.

This developed standard gas generation equipment will be sold from Gastec. Co. Ltd.. (6431, Fukaya, Ayase city, Kanagawa pref., 252-1103, Japan)

Figure 2 shows principle of gas generation by using the diffusion tube. Points of this method were small diameter (0.2–1.0mm) of the diffusion tube and a sample injection method. The concentration of gas can be controlled by area and length of the diffusion tube, temperature and flow rate of dilution gas by the following equation (1)[1].

$$C = \frac{A \cdot D \cdot M \cdot P}{F \cdot L \cdot R \cdot (273+t)} \ln\left(\frac{P}{P-Ps}\right) \times 6 \times 10^4 \cdots (1)$$

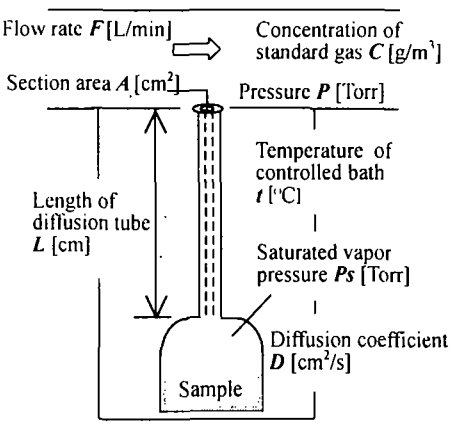

Figure 2 Principle of gas generation by using diffusion tube

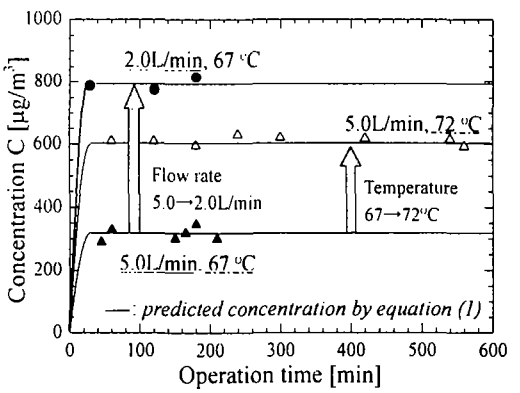

Figure 3 Examples of accuracy and stability of generation concentration (2,4,6-trichlorophenol)

Results and Discussion

Basic performance of the equipment

Figure 3 shows the accuracy and stability of generated concentration of 2,4,6-trichloro-phenol whose vapor pressure was known. Though the flow rate and the temperature were changed, the concentrations were stable within ±5%. From these results, it was confirmed that the temperature and the flow rate of this equipment were stable and reliable.

Figure 4 shows the results of examination for cleanup performance of hexachloro-dibenzofuran (H_6CDF) and

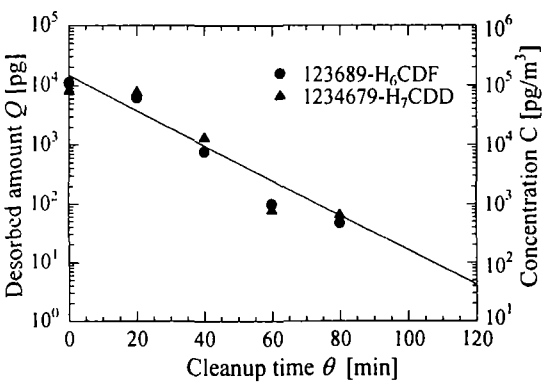

Figure 4 Examples of cleanup performance of sticked H_7CDD/H_6CDF (200°C, 5.0mL/min)

heptachloro-dibenzo-*p*-dioxin (H_7CDD) which were sticked easily in the equipment because of their low vapor pressure. It was found that residual ratio of these compounds could be decreased under one thousand in 2-hours, and could be expressed by an equation (2). Therefore, the residual ratio of PCDDs/PCDFs and related compounds might be cleaned up within the time calculated by the equation (2).

$$\log(Q/Q_0) = -3.0\times10^{-2}\cdot\theta \quad \cdots(2)$$

Q : desorbed amount [pg], θ : cleanup time [min]

Prediction method of generation gas concentration

The diffusion coefficient D and the vapor pressure Ps are necessary for prediction of the generation concentration by the equation (1).

It was known that relation between the diffusion coefficient and molecular weight M and pressure P is shown theoretically by an equation (3). And change of the diffusion coefficient D with temperature could be estimated empirically by an equation (4). Then the diffusion coefficient of the objective compounds could be obtained from a diffusion coefficient D' [cm^2/s] of similar compound at 25 [°C] and 760 [Torr] by an equation (5).

$$D = \beta / P\cdot\sqrt{M} \quad \cdots(3)$$

$$D = \alpha(273+t)^{1.833} \quad \cdots(4)$$

$$D = D'\sqrt{\frac{M'}{M}}\left(\frac{273+t}{298}\right)^{1.833}\left(\frac{760}{P}\right) \quad \cdots(5)$$

As shown in Figure 5, the prediction concentrations of tetrachlorobenzene and pentachlorophenol, whose vapor pressure values were obtained from the Antoine equation[2], agreed well with the measured data in the temperature higher than their melting points. These results show that this gas generation equipment was reliable. Moreover, it was confirmed that the diffusion coefficient could be estimated well by the equation (5). Therefore, the generation gas concentration can be estimated precisely by the equation (1), if vapor pressure is obtained. But the measured data under the melting point

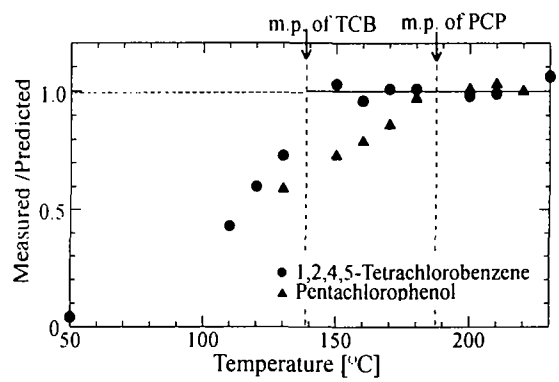

Figure 5 Comparison of measured concentration and predicted concentration estimated by equations (1), (5) and the Antoine equation

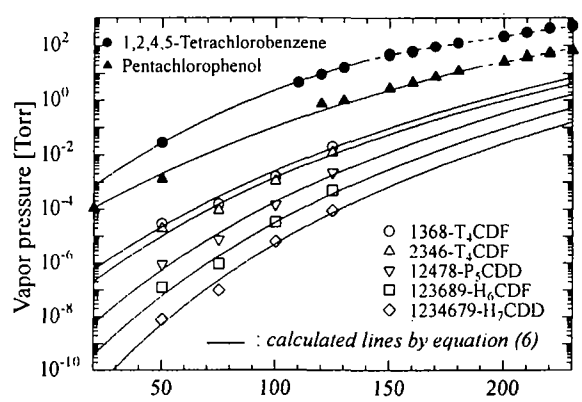

Figure 6 Estimation of vapor pressure of PCDDs/PCDFs. CBZ and CP

were disagree with the predicted concentration by using vapor pressure from the Antoine equation for liquid. So, estimation method of vapor pressure for solid compounds such as PCDDs/PCDFs was examined. We found that the vapor pressure *Ps* at a temperature *t* could be estimated by an equation (6) for solid compounds like the Antoine equation, but parameters (a,b and c) were different from the parameters of the Antoine equation for liquid.

$$\log Ps = a - \frac{b}{c+t} \quad \cdots(6)$$

If vapor pressure of solid compounds at optional temperature can be shown by the equation (6), the parameters of a, b, c can be obtained from three data or more. And in case of compounds whose boiling points are known, 760 Torr becomes one data at their boiling points.

Examples of change of the vapor pressure of PCDDs/PCDFs, tetrachlorobenzene and pentachlorophenol with temperature are shown in Figure 6. The calculated lines by the equation (6) fitted to the all measured data. It was confirmed that the vapor pressure of solid compounds at optional temperature could be estimated by the equation (6). Therefore, we could predict and control the concentration of dioxins and related compounds by the equations (1), (5) and (6).

Concentration range of generation gas and precision of the prediction

Figure 7 shows comparison between the measured concentrations with the predicted concentrations of dioxins and related compounds. From these results, it was clarified that these compounds could be generated in extremely wide concentration range from ambient level to flue gas level. And it was confirmed that the generation concentration could be predicted in an error range under 1/2 to 2 times of the calculated values until the very low concentrations as 10^{-12}g/m^3. Since this equipment is able to use four diffusion tube at once, the mixed standard gas of four compounds can be generated.

By using this equipment, various research and development for countermeasures to dioxins may be promoted extremely. For examples, researches for formation mechanism of dioxins on fly ash and developments of decomposition or removal technologies of dioxins by catalyses or activated carbons etc. Furthermore, the collection efficiencies of dioxins in various measuring methods can evaluate by using this equipment.

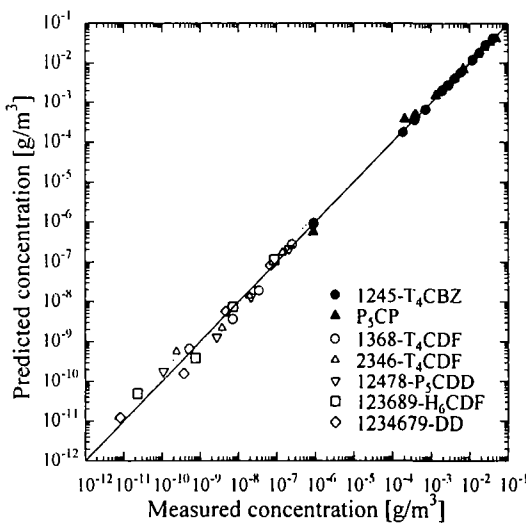

Figure 7 Comparison between measured concentrations and predicted concentrations of PCDDs/Fs and related compounds

References

1) G.A. Lugg. (1986), *Anal. Chem.*, 40, 1072.
2) John A.Dean, (1985). Lange's handbook of chemistry 13th, McGraw-Hill.