STABLE AND ADJUSTABLE GASEOUS 2,3-DCDD DIOXIN SOURCE FOR LABORATORY SCALE ADSORPTION

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Introduction

In many countries, authorities set a very low emission rate of dioxin for waste incinerator plants (0.1 ng I-TEQ.Nm^{-3}), requiring a long and consequently expensive method comprising sampling, extraction/purification and identification/quantification stages. Our research team is currently working on an on-line and real time analysis laboratory device, using zeolite instead of standard XAD-2 resin in a selective pre-concentrator device, in order to gain sensitivity for subsequently gas chromatography/mass analysis. The qualification of such a device in adsorption experiments requires a gaseous dioxin source which is stable in time, adjustable in flow rate and concentration and predictable.

In literature, many ways are used to perform dioxin adsorption. Most of them dissolve dioxin in solvent, then, an adsorbent is brought in contact with the solution[1], or the solution is spiked on the input of the sorbent column, which is then heated and flushed by an inert gas[2,3]. Some authors used borosilicate beads coated with dioxin, inserted in a glass vessel, with a known gas volume[4]. The gaseous dioxin volume is limited by the vessel size. Jager et al.[5] describes another method for dynamic gas phase adsorption from flying ashes: it consists on the extraction of dioxin contains in fly ashes and then in the impregnation of amorphous silica. None of these methods can offer a long-term stable dioxin gaseous source nor are suitable for dynamic gas phase adsorption experiments.

Dioxins are low volatility compounds. To avoid re condensation and obtain a steady dioxin flow, a dynamic generation device is necessary. As the commercially available devices for permeation are not suitable for dioxins, we developed our own generation system. 2,3-DCDD is used: it can simulate Seveso dioxin for micro-pore adsorption in the zeolites, as they possess the same size, and it is not toxic.

Materials and methods

The generation device consists in two glass vessels, one dedicated to actual generation and the other one to dilution. Both vessels are equipped with a gas supply (cf. Fig 1.).

The two flow rates of input gas are set up and measured by two distinct mass flow meters (Bronkhorst ElFlow Select, 0-200 mL.min^{-1} and Bronkhorst ElFlow Select, 0-500 mL.min^{-1}).

A third mass flow meter can be added, to split the flow coming from generation glass vessel, to reach low concentration.

The generation cell contains about 2.5 mg of solid 2,3-DCDD flakes and it is put in the first glass vessel. This cell consists of a glass vial (2 mL) containing pure dioxin in a solid state closed with a porous PTFE membrane with a porosity of 0.6 and pore diameter of 10 µm (Millipore).

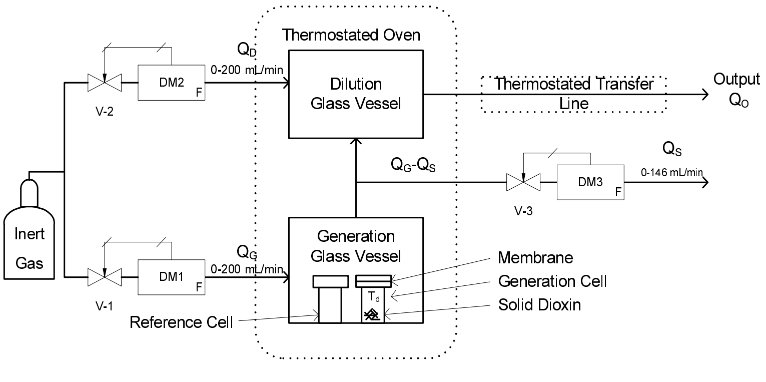

Figure 1: Gaseous dioxin generator principle

The whole system, except the flow meters and the valve are set in a thermostated oven (Memmert UFP400) in order to keep the temperature stable. The cell is weighed regularly (every two day) by means of an analytical balance (Sartorius CP225D-OCE, 0.01 mg of resolution from 0 to 80 g). A reference vial is weighed to warn a drift from the balance. Before weighing, both vials are cooled down for 10 min at ambient temperature. The mass of generated dioxin is directly determined from the mass loss (Δm) of the generation cell. The generation rate ($q_D = \frac{\Delta m}{\Delta t}$, mg.min^{-1}) of dioxin is determined after a minimum of one week of measurement. Output concentration C_{diox} (mg.m^{-3}) is calculated from q_D and the different flows, Q_G, Q_D, Q_S and Q_O (with $Q_O = Q_G - Q_S + Q_D$, m^3):

$$C_{dioxin} = \frac{q_D}{Q_G} \times \left(\frac{Q_G - Q_S}{Q_O} \right)$$

This generation system is not conventional, so the physical principles will be detailed according to three steps:

- dioxin sublimation,
- binary diffusion of the dioxin in the gas contained in the generation cell (Fick's law),
- diffusion through the membrane's pores (Hagen Poiseuille flow).

Sublimation is related to vapour pressure which varies with temperature, then, binary diffusion depends on the nature of the gas and on the temperature and pressure of the system. Finally, the diffusion through the porous membrane is related to the membrane characteristics and to the difference of the partial pressure between the two sides of the membrane.

The influence of four parameters is evaluated: temperature, pressure, flow rate and gas nature, to ensure that our model fits the experiments.

Results and discussion

The generation flow rate influence is tested by making Q_G vary from 20 to 200 mL.min^{-1}. For Q_G ranges from 50 to 200 mL.min^{-1}, generation rate is considered constant (76 - 84 µg.day^{-1}); but for lower Q_G values, the generation rate is smaller and not constant in time.

When the oven temperature varies from 75 to 125 °C, the higher the temperature, the greater the generation rate. For instance, at 95 °C, q_D equals 88 µg.day^{-1}.

The system pressure has also an influence on generation rate. If generation is carried out at atmospheric pressure, dioxin gas phase is three times higher than at 2 bars.

Previously experiments are carried out with Nitrogen as carrier gas. With helium, the generation rate is five times higher than with Nitrogen.

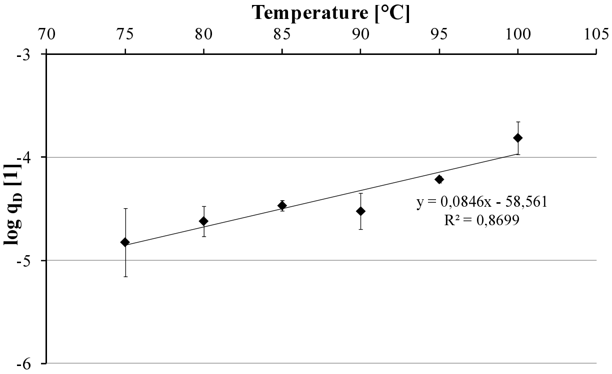

Figure 2 : Generation rate versus oven temperature (semi logarithmic representation)

The influence of these three parameters (temperature, system pressure and carrier gas nature) signifies the generation is mainly related to binary diffusion.

Different generation cells are used, with same parameters (2 bars, 95 °C, nitrogen, $Q_G \geq 50$ mL.min^{-1}). The average q_D is 88 µg.day^{-1} ± 25 %. The dispersion of the results may come from the membrane (a new membrane is used for each generation cell) and/or different arrangements and shapes of the dioxin flakes.

The binary diffusion coefficients of 2,3-DCDD in the carrier gas, D, determined with our system are close to those theoretically calculated[6] for a cylinder. The discrepancy between these values comes from the cell geometry which is not a real cylinder (Table 1)

Gas Nature	System Pressure [Bar]	System Temperature [°C]	Experimental D [$m^2.s^{-1}$]	Theoretical D [$m^2.s^{-1}$]
Nitrogen	2	75	$3.48.10^{-6}$	$5,28.10^{-6}$
Nitrogen	2	80	$3,36.10^{-6}$	$5,39.10^{-6}$
Nitrogen	2	85	$2,90.10^{-6}$	$5,51.10^{-6}$
Nitrogen	2	90	$1,59.10^{-6}$	$5,62.10^{-6}$
Nitrogen	2	95	$2,03.10^{-6}$	$5,74.10^{-6}$
Nitrogen	2	100	$3,59.10^{-6}$	$5,86.10^{-6}$
Nitrogen	1	95	$6,67.10^{-6}$	$1,13.10^{-5}$
Helium	2	95	$9,24.10^{-6}$	$2,38.10^{-5}$

Table 1: Diffusion coefficients of 2,3-DCDD for several conditions

The third flow meter is used to divide the generation flow to dilute and consequently decrease the gaseous dioxin concentration. Hence, for a constant flow rate, different concentrations are available. Likewise, if a set concentration is needed, the outlet flow rate can vary (Table 2).

Generation flowrate [$mL.min^{-1}$]	Split flowrate [$mL.min^{-1}$]	Dilution flowrate [$mL.min^{-1}$]	Outlet flowrate [$mL.min^{-1}$]	Outlet concentration [$\mu g.m^{-3}$]
Constant outlet flowrate				
200	0	0	200	277
200	40	40	200	222
200	80	80	200	166
200	120	120	200	111
200	140	140	200	83
200	160	160	200	55
200	180	180	200	28
200	200	200	200	0
Constant outlet concentration				
200	100	100	200	139
175	98	98	175	139
150	93	93	150	140
100	75	75	100	139
75	61	61	75	138

Table 2: Outlet flow rate and concentration ranges obtained with the split flow meter

After each flow rate modification, a stabilization period of only few hours is needed. A single generation cell enables 2 to 3 weeks adsorption experiments, with a constant generation rate.

Then, the flow of carrier gas with dioxin can be driven to either a sampling loop for GC/MS quantification or sorbent tube for adsorption characterizations by means of valves and transfer lines. All are maintained at high temperature (250 to 270 °C) and their inner parts are coated with deactivated silica to minimize or avoid condensation.

To conclude, our standard generator is adapted to perform adsorption experiments. The outlet flow rate and concentration are adjustable independently and the entire device is designed to avoid dioxin condensation. The dioxin generator can naturally be used with another dioxin or with 2 or 3 dioxins together, with a parameters adjustment. Moreover, this system can easily evolve. More gases like CO_2, O_2 or H_2O can be added to be closer of waste incinerator gaseous emissions. Influence of the gaseous matrix on adsorption will be determined.

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