

Gas/Particle Partitioning of PCDD/F in the Flue Gas of Waste Incineration Plants

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1. Introduction

In the flue gas of waste incineration plants polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) occur both in the gasphase and attached to particles. The physical state of the PCDD/F in the flue gas is important for the selection and efficiency of purification systems to reduce these compounds.

In several studies the partitioning of organic compounds to the gas- and particulate phase in the atmosphere and its dependence from different parameters, e.g. vapor pressure and temperature was examined ¹⁾⁻⁴⁾. Based on the physical adsorption theory a theoretical model can be derived to describe the gas/particle partitioning. At two waste incineration plants measurements were performed to investigate the partitioning of the PCDD/F in the flue gas.

2. Theory

Using the physical model of single compound adsorption in form of a linear Langmuir-isotherm, the following equation can be derived to describe the gas/particle partitioning:

$$\frac{C_G}{C_P} = \frac{1}{c \cdot \Theta} \cdot p^0 \quad (1)$$

$$\text{with } c = \frac{m_w^*}{M} \cdot b_L \cdot R \cdot T$$

C_G : Concentration of the compound in the gasphase [ng/m³]

C_P : Concentration of the compound attached to particles [ng/m³]

p^0 : Saturation vapor pressure [Pa]

Θ : Solid surface area in the gas volume [m²/m³]

m_w^* : Mass-amount of the compound at monomolecular surface covering [g/m²]

b_L : Langmuir-constant

R : Gas constant [J/mol K]

T: Temperature [K]
M: Molecular weight [g/mol]

The parameter c is a function of temperature and different compound parameters. The solid surface area Θ is a function of the particle sizing, the form of the particles and the porosity. In the case that c is constant for the group of PCDD/F at a given temperature, the gas/particle partitioning described by equation (1) is a linear function of the saturation vapor pressure.

3. Experimental

The isokinetic sampling for representative particle separation was performed in the flue gas behind a scrubber at gas temperatures of 65°C. A part of the main flue gas volume was diverted through a particle filter of stuffed quartz fiber, placed on several positions in the flue gas duct during sampling. The aqueous compounds of the gas sample were condensed outside the duct in a cooler and the gaseous compounds were adsorbed in a XAD-2 cartridge. During a period of 6 hours a gas volume of approximately 15 m³ was collected. The preparation and analysis of the two sample parts, filter (index F) and condensate/XAD-2 (index K), occurred in the laboratory. The quantification of the PCDD/F was performed on a HRGC/HRMS-System (Carlo-Erba/VG Autospec). 16 congeners of the PCDD/F with chloratoms in 2,3,7,8-position and the homologues Tetra - Octa were analysed.

4. Results and Discussion

For example the relation between the concentrations in the condensed/adsorbed sample C_K and the filter sample C_F are given in figure 1 in form of a plot over the saturation vapor pressure of the PCDD/F congeners. The values of the saturation vapor pressures were extrapolated using data from RORDORF⁵⁾. Because of the large range of the values, the logarithmic scale was chosen.

In the filter sample (F) generally small parts of PCDD/F were found. With increasing saturation vapor pressure the amount of the condensed/adsorbed sample (K) increases. The transformation of eq. (1) leads to following linear equation with a theoretical value for the slope of $m=1$.

$$\log \frac{C_K}{C_F} = m \cdot \log p^0 - \log(c \cdot \Theta) \quad (2)$$

The linear regression of the measured values in figure 1 shows a good correlation. The slope of the regression line lies with $m=0,71$ below the theoretical value of 1. For the product of $c \cdot \Theta$ a value of $2,1 \cdot 10^{-4}$ Pa was determined.

Other series of measurements led to similar results, with slopes always $m < 1$. For the homologues an analysis can be performed as well, using the mean values of the vapor pressures of the congeners. The regression results of the measurements are given in table 1. The slopes of the homologues are more or less greater than the slopes of the

congeners. The product of $c \cdot \Theta$ varies within two magnitudes. Sample 3 shows the greatest deviation and a poor correlation.

The differences between the results of the samples in table 1 cannot be attributed to single parameters, because of the multiple influences in the incinerator and flue gas purification processes. A comparison of the gas/particle partitioning to the amount of the dust loading of the flue gas leads to no correlation, do to the relatively small variation of the measured values. An important factor is the structure of the particles and the particle sizing which mainly determine the solid surface area.

In comparison to the theoretical value of 1, the lower values of the slopes indicate that the particulate phase is overestimated for the congeners with high saturation vapor pressures or underestimated for the congeners with low saturation vapor pressures. The theoretical model provided that the parameter c is constant and independent of the single congeners. On the assumption that Θ is constant, the slopes < 1 indicate that c increases with increasing saturation vapor pressure. This means that the congeners with higher saturation vapor pressure are stronger attached to the particles.

Another influence on the gas/particle partitioning is the occurrence of so called "non-exchangeable" parts which do not interact with the gasphase⁶⁾. In this case the results indicate an increasing of the particulate phase with increasing vapor pressure.

The occurrence of artifacts during sampling must also be considered. The theory of the gas/particle partitioning based on the physical equilibrium between the two phases. The interaction of the separated particles with the gasphase during sampling can influence the partitioning and depends on kinetic properties. Providing an adsorption of the congeners from the gasphase to the separated particles, the lower slopes indicate a faster adsorption of the congeners with higher vapor pressures.

5. References

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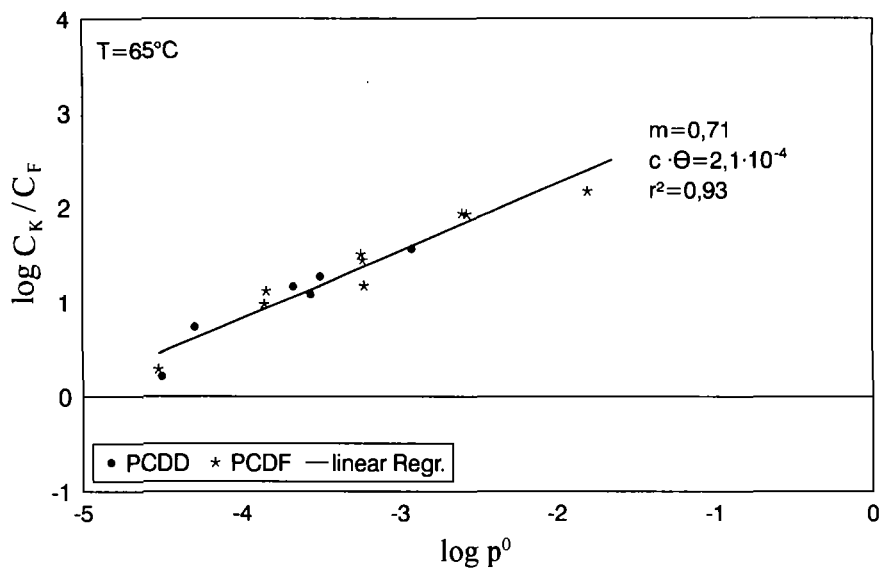


Fig. 1: Gas/particle partitioning of the PCDD/F congeners

Sample	Congeners			Homologues		
	m	c·Θ Pa	Correlation r^2	m	c·Θ Pa	Correlation r^2
1	0,71	$2,1 \cdot 10^{-4}$	0,93	0,85	$5,3 \cdot 10^{-5}$	0,98
2	0,76	$1,6 \cdot 10^{-4}$	0,88	0,98	$1,8 \cdot 10^{-5}$	0,96
3	0,32	$3,7 \cdot 10^{-2}$	0,54	0,40	$1,8 \cdot 10^{-2}$	0,84
4	0,59	$4,2 \cdot 10^{-4}$	0,95	0,63	$2,6 \cdot 10^{-4}$	0,96
5	0,50	$4,6 \cdot 10^{-4}$	0,83	0,60	$1,8 \cdot 10^{-4}$	0,93
6	0,73	$3,9 \cdot 10^{-5}$	0,92	0,79	$2,1 \cdot 10^{-5}$	0,96
7	0,71	$4,6 \cdot 10^{-5}$	0,95	0,78	$2,1 \cdot 10^{-5}$	0,95

Tab. 1: Regression parameters

