PCDD/F GAS/PARTICLE PARTITIONING AND ITS RELEVANCE IN GAS CLEANING PROCESSES AND IN MECHANISTIC STUDIES (I)

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Introduction

Gas/particle partitioning of PCDD/F plays a cardinal role in adsorption and filtration (during the cleaning of flue gases from PCDD/F), as well as in atmospheric processes, in dry and wet deposition, long-range transport, or decomposition by photolytic and radical reactions[1]. Partitioning is influenced by temperature, vapour pressure, surface properties of particles and nature of the compounds[2→9]. The following equation has been used successfully to describe gas/particle partitioning[1]:

$$K_p = \frac{C_{p_l}/TSP}{C_G} = \frac{1}{\alpha . TSP}$$

where K_p (m^3/g) is a temperature dependent partition constant, TSP (g/m^3) the concentration of total suspended matter, and C_p, C_G (ng/m^3) are the particle associated and the gaseous concentrations of the compound considered. Plotting K_p against the sub cooled liquid vapour pressure p_L gives a linear equation, or when represented in a log/log plot:

$$\log K_p = m . \log p_L + b$$

The question has been raised in how far PCDD/F are either solidly held by particle, or freely exchangeable between phases. Analysis of the scarce atmospheric data provides evidence for an exchangeable transfer of PCDD/F. The non-exchangeable fraction has been associated with the soot (and organic) fraction of the (atmospheric) aerosol[1]. It is well-known from earlier Minidip-studies that MSW-incinerator ash often holds PCDD/F extremely well, even at 300 °C; metallurgical dust, on the contrary is but a poor adsorbent, even below 100 °C[9].

The following equation links α, the dimensionless ratio of the concentration of the compound in the gas phase to that in the particle phase, with vapour pressure, on the basis of a Langmuir-isotherm adsorption equilibrium[7]:

$$\alpha = \frac{C_G}{C_p} = \frac{1}{c . \Theta} . p^0 \qquad with \quad c = \frac{m^*_\infty}{M} \cdot b_L \cdot R \cdot T$$

C_G : Concentration of the compound in the gas phase (ng/m^3)
C_p : Concentration of the compound attached to particles (ng/m^3)
p^0 : Saturation vapour pressure (Pa)
Θ : Solid surface area in the gas volume (m^2/m^3)
m^*_∞ : Mass-amount of the compound at a monomolecular surface covering (g/m^3)
b_L : Langmuir-constant
T : Temperature (K)
R : Gas constant (J/mol K)
M : Molecular weight (g/mol)

Smolka and Schmidt[7] investigated such a distribution in the flue gas of a waste incinerator, up and downstream of an activated carbon filter. In such a unit PCDD/F-laden particles are first separated by filtration and then adsorb more PCDD/F from the gas flowing through the filtered dust. In the data examined a distinction was made between an incinerator fly ash capable of firmly holding all PCDD/F, and that from another plant, in which this distribution was fairly even between the two phases. The latter is typical for recent plant, with a deep carbon burn out. Attention is paid to the partition parameters α and K_p, to their (limited) reproducibility during de novo tests and (in part II) in industrial plant, and the way they are both influenced by the presence of adsorbents or of other gas cleaning agents, mainly hydrated lime. In this paper a selection is made from a much wider variety of relevant gas/particle partitioning data, that were gathered during the Minidip project as well as in various confidential study assignments, and conclusions are reached regarding the practical value of the correlations, based on K_p, α, or on a third equation derived from a Langmuir adsorption equilibrium:

$$TSP.\alpha = 1/K_p + C$$

Materials and Methods: Experimental.

Several type of experimental data were used in this study: (1) retention times of model compounds (hexane, MCBz, MCPh, ...) on a series of short isothermal adsorption columns, (2) de novo tests and the gas/particle partitioning of the compounds arising in this test, and in part II of this paper (3) industrial plant PCDD/F-data, obtained with a separate preparation and analysis of filter and cartridge PCDD/F.

Results

First, the adsorption of simple model compounds (hexane, MCBz, MCPh) on a short adsorption column was studied for a series of conventional chromatographic carriers (NaY Zeocat, Aerosil fumed silica, Siralox silicoaluminate, sorbalit), in order to establish a data base for comparison with actual samples of process dust. Values for the activation energy E were derived from a comparison of retention times obtained in a temperature range from 100 to 400 °C. Figure 1 shows the Arrhenius diagram of chlorobenzene and chlorophenol on zeolite NaY. The values for E are in a range, corresponding to adsorption. In some cases the activation energy decreases towards low values at high temperature, possibly pointing at transfer limitations. Table 1 lists a few results.

Column	Compound	Temp. Range, °C	Arrhenius Correlation	R^2
NaY	n-hexane	100 – 200	0.513 x – 11.990	0.98
		270 – 400	0.136 x – 5.072	0.58
	chlorobenzene	200 – 300	0.768 x – 14.537	0.996
	2-chlorophenol	325 – 400	0.808 x – 11.731	0.96

Table 1: Arrhenius correlation for three compounds, adsorbed on NaY Zeocat

During the last years, in a collaborative effort of FZ-Karlsruhe and VUB, numerous de novo tests were conducted on filter dust and other particle collected from metallurgical or incinerator plant. From the (dimensionless) gas/particle partition obtained by separate analysis of both the treated dust and the carrier gas flow chloroaromatics the adsorptivity of the dust tested for PCDD/F, PCBz, PCPh, PCB, and PAH was derived for numerous samples. Comparing the partition parameter for various temperatures allowed to derive an E-value, characteristic for chemical reaction[10]. Some other conclusions of such work are:

a) the de novo formation potential of samples from two metallurgical smelter (B and C) was studied; the two samples, from different units, and from different locations in these units (dust, separated in-process, at still high a temperature, and dust from a baghouse filter, after injection of lime and lignite coke), show a very distinct behaviour,

b) the first sample (plant B) had only low initial load; the latter augmented slightly during the annealing test. The second (plant C) was highly loaded initially, due in part to the presence of lignite coke adsorbent; after annealing it had a much lower residual load left. In both cases, however, the sequence in both their de novo generation potential and their α volatility is the same: PCBz > PCB > I-TEQ > PCPh,

c) the de novo formation was also compared with plant emission data, as well as analyses of filter dust. These confirmed that the main PCDD-precursor, PCPh, is effectively retained by hydrated lime, largely preventing emission of this PCDD-precursor.

Sample	**Original Load**		**Plant B, after annealing at 300°C**		**Plant C, after annealing at 300°C**		
	Plant B	**Plant C**	**dust**	**gas**	**dust**	**gas**	**unit**
TE	0.23	38.7	3.25	5.27	0.0637	0.260	ng TE/g
PCDD	1.18	626	35.35	34.1	0.525	1.894	ng /g
PCDF	5.61	859	62.44	159.5	1.787	7.039	ng /g
PCBz	4.24	272	80.6	4176	4.74	111	ng /g
PCB	2.23	1025	40.2	430	8.57	13.3	ng /g
PCPh	10.76	1565	121.7	0	0.94	6.49	ng /g

Table 2: Chloroaromatics load, before annealing, and dust/gas partition after annealing

In principle, the carbon fragments set free in a de novo test consist of (aliphatic and) aromatic structures, which in the process of formation either report to the gas phase, or are adsorbed. Thus, an analysis of the gas/particle distribution, obtained by a de novo test, yields precious data on what actually happens during de novo formation. From an investigation of a large number of industrial dust samples two types of dust can be identified: a) some (plant C) that effectively partition the PCDD/F formed over the gas and solids phase, according to their relative volatility (i.e. OCDD/F are much better adsorbed than TCDD/F), whereas other samples (plant B) do not show much of such a preferential order. In the latter case the partition is determined solely by de novo reaction, barely influenced by vapour pressure or adsorption equilibrium. A similar distinction was observed during testing on actual industrial plant and separate analysis of both phases.

Figure 2 shows the results for individual PCDD/F and PCB-homolog classes, and PCBz for plant B. Plant C shows only little dependence of partition on vapour pressure. Figure 3 similarly represents a filter dust from a sintering plant.

Conclusions

Several methods were tested to describe the partition of PCDD/F between gas and particle phase, both on plant data (part II), and in a de novo laboratory test, as developed by Dr Stieglitz (FZ-Karlsruhe). In these tests some dusts generate a gas/dust partition, that follows vapour pressure, whereas others do not. The result may be different for PCDD/F and for PCB or PCBz; it is more influenced by decomposition of the chlorinated carbon structure than by gas/solids partition. Adsorption tests were conducted on a chromatographic column, to provide a reference base for evaluating the adsorptivity of dust samples from actual metallurgical or incinerator plant.

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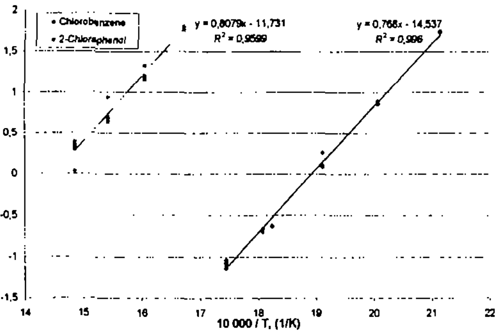
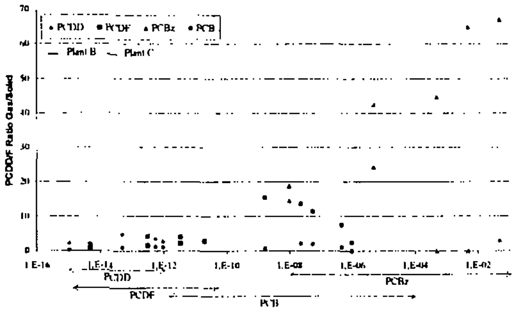


Figure 1: Arrhenius diagram, established on the basis of adsorption tests: MCBz and MCPh on NaY



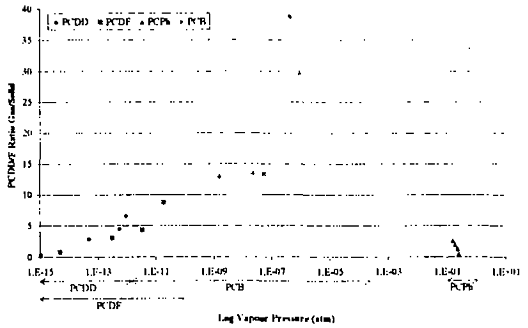


Figure 2: plant B & C, ratio of gas phase to residual dust PCDD/F, PCB, PCBz as a function of vapour pressure

Figure 3: sintering plant EF dust, ratio of gas phase to residual dust PCDD/F, PCB, PCBz, PCPh as a function of vapour pressure