

FORMATION OF PCDD, PCDF, PCBz, PAH AND PCB IN A PILOT
INCINERATOR.

Fångmark I.^A, van Bavel B.^A, Marklund S.^A, Rappe C.^A, Strömberg B.^B and Berge N.^B.

^A Institute of Environmental Chemistry, University of Umeå, S-901 87 Umeå, SWEDEN.

^B Studsvik AB, S-611 82 Nyköping, SWEDEN

INTRODUCTION

In a previous study we have reported on experiments conducted in order to find the parameters of importance for the formation of polychlorinated dioxins (PCDDs) and furans (PCDFs) during combustion¹. The experiments were performed in a laboratory scale fluidized bed reactor². The objective of the study was primarily to find the operation parameters that minimize the emission of PCDDs and PCDFs, but a second objective was to investigate the formation of other organic micropollutants.

The flue gas samples collected for the analysis of PCDDs and PCDFs were divided, after extraction, into two parts. The second part was analyzed for chlorinated benzenes (PCBz), polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCBs). These analytical data together with the PCDDs and PCDFs and the operation parameters were used in a principle component analysis (PCA) in order to find the parameters of importance for minimizing the formation of all these compounds during combustion.

MATERIALS AND METHODS

Reactor and fuel

A small scale fluidized bed reactor (diameter 0.1m, height 1 m) capable of burning around 1 kg of pelletized refuse per hour was used for the experiments. The reactor top is connected to a cooling section where the flue gas temperature profile can be varied by cooling, insulating or electric heating. The cooling section has two sampling ports so that flue gas samples with different residence times in the cooling section can be collected. To minimize variations in fuel composition a synthetic fuel made from common laboratory chemicals was used in the experiments. The total chlorine concentration in the fuel is 0.7 % by analysis. A detailed description of the reactor and the fuel is given elsewhere^{1,2}.

Combustion parameters and experimental plan

The following combustion parameters were studied: bed temperature (T_{bed}), oxygen concentration (O_2), flue gas temperature at sampling point (T_{sampl}), residence time in the cooling section (Time), concentration of HCl (HCl) and concentration of H_2O (H_2O). HCl and H_2O were added to the primary air during combustion.

To estimate the influence of these parameters on the yield of PCDDs, PCDFs, PCBz, PAHs and PCBs a multivariate approach was used in the design of the screening experiments. All parameters were studied on two levels which were chosen to give a significant difference in yield. Still the parameters were chosen to fit in or be close to the range found in practical operation. The experimental plan of two level fractional factorial design is presented in Table 1 and the levels and standard deviation obtained in Table 2.

Table 1. Experimental plan (+ = high level, - = low level).

Experiment number	HCl	T_{bed}	O_2	T_{sampl}	H_2O	Time
1	+	-	-	-	+	-
2	+	+	-	-	+	+
3	+	-	+	-	-	+
4	+	+	+	-	-	-
5	+	-	-	+	-	+
6	+	+	-	+	-	-
7	+	-	+	+	+	-
8	+	+	+	+	+	+
9	-	-	-	-	+	-
10	-	+	-	-	+	+
11	-	-	+	-	-	+
12	-	+	+	-	-	-
13	-	-	-	+	-	+
14	-	+	-	+	-	-
15	-	-	+	+	+	-
16	-	+	+	+	+	+

Table 2. Parameters tested and levels \pm standard deviations obtained between experiments.

Parameter	Low level (-)	High level(+)
T_{bed} ($^{\circ}C$)	760 ± 8	874 ± 4
O_2 (%)	4.9 ± 0.5	7.5 ± 0.5
T_{sampl} ($^{\circ}C$)	264 ± 35	456 ± 16
Time (sec) *	0.6 ± 0.1	1.6 ± 0.3
HCl (g/h)	0**	10.2
H_2O (g/h)	0**	136.5

*) Calculated from total air supply, gas composition and local temperatures.

***) The low level means no additional HCl or H_2O supplied apart from what is formed from the fuel. Feeding 1.1 kg fuel /h will theoretically form 8 g HCl/h.

Sampling, analysis and data treatment

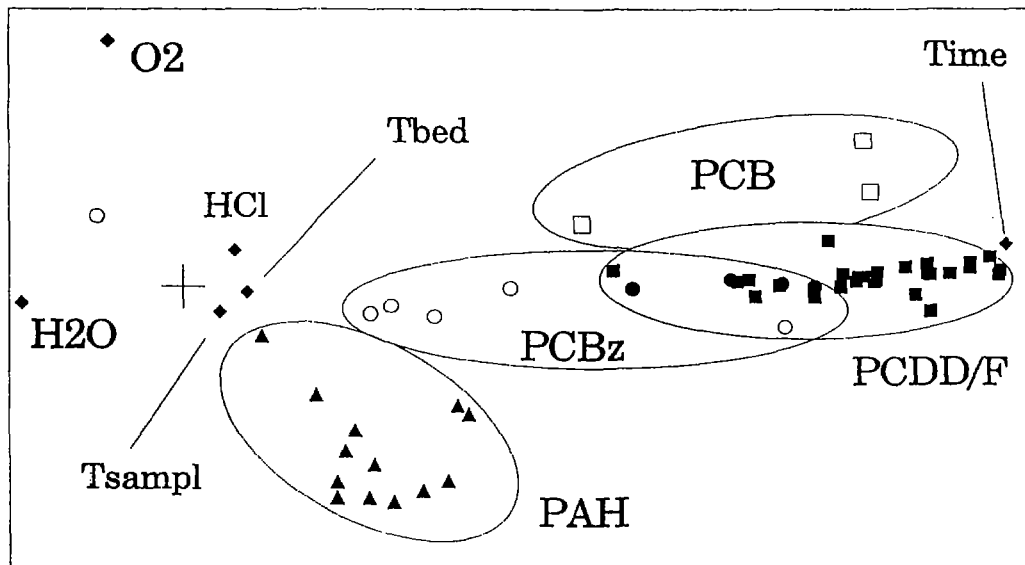
A sampling technique based on a cooled probe was used in order to avoid chemical reactions in the sampler. The cooled probe - polyurethane foam plug sampling technique is described elsewhere³. All flue gas samples were collected isokinetically and ¹³C labelled sampling spikes of PCDDs and PCDFs were added to the sampling train before start up. Sample clean up and analysis of PCDDs and PCDFs on HRGC-HRMS were made according to Marklund⁴. Clean up and analysis of PCBz, PAH and PCB were made according to van Bavel⁵. For PCDD and PCDF all toxic isomers and the sums of each congener group were quantified. For PAH the following compounds were analyzed: naphthalene, fluorene, phenanthrene, anthracene, fluoranthrene, benzo(a)pyrene, indenopyrene, benzoperylene, dibenzoanthracene and anthracene. Ten chlorinated benzenes (PCBz) from dichloro up to hexachloro and three PCBs, IUPAC-number 77, 126 and 169, were analyzed.

Operation parameters together with all analytical results obtained, i.e. 27 PCDD/PCDF, 13 PAH, 10 PCBz and 3 PCBs, were used as input in a principle component analysis (PCA), Wold et al⁶.

RESULTS AND DISCUSSION

Two significant principle components explain 62 % of the total variance in the data set. It is evident from the loading plot, Figure 1, that there is a correlation between all the chlorinated compounds, PCDD, PCDF, PCBz, PCB and the residence time in the cooling section. This indicates that all of these chlorinated compounds are produced in the post combustion zone. For the lower chlorinated isomers of PCBz (open rings in the plot) the correlation is less good. The explanation for this could be that the formation of these higher vapor pressure compounds is dominated by other, not catalytical, reaction mechanisms such as gas phase reactions. Another possibility is that these data suffer from a systematic error due to evaporation losses of the more volatile isomers during sampling and clean-up. It is also evident that there is no correlation between the chlorinated compounds and the PAHs indicating that there are different mechanisms involved in the formation of polyaromatic hydrocarbons and chlorinated hydrocarbons. The parameter mainly responsible for the formation of PAHs is the oxygen content in the flame. This supports the theory that PAH are formed during oxygen deficient conditions. Apart from the residence time and the O₂ concentration none of the other operation parameters seem to be important for the formation of any of these compounds.

Figure 1. Plot of the variable loadings for the first two principle components (◆ = parameters, ■ = PCDD, PCDF, ○ = di- and trichlorinated PCBz, ● = tetra- to hexachlorinated PCBz, ▲ = PAH, □ = PCB).



REFERENCES

1. Fångmark I., Marklund S., Rappe C., Strömberg B., Berge N. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, part II. *Chemosphere* 23, (1992), 1233 - 1243.
2. Marklund s., Fångmark I., Rappe C., Berge N., Strömberg B. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, part I. *Chemosphere*, 20, (1990), 10-12, 1859-1866.
3. Fångmark I., Wikström L-E., Marklund S., Rappe C. Studies on sampling methods for PCDDs and PCDFs in stack emission. *Chemosphere*, 20, (1990), 1333 - 1340.
4. Marklund S. Dioxin emission and environmental imission. Thesis, University of Umeå, 1990.
5. van Bavel B., Fångmark I., Marklund S., Söderström G., Ljung K., Rappe C. Quantitative analysis of trace organic compounds by isotope dilution: formation of planar PCBs during incineration. *Dioxin* 92, this issue.
6. Wold S., Esbensen K. and Geladi P. Principle component analysis. *Chemom. Intell Lab Syst.* 2, (1987), 37-52.