

## Isokinetic Sampling of PCDD/F Response in Low and High Volatile Fractions of a Wood Incinerator

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### Introduction

Incomplete combustion of wood treated with preservatives and plastic layers can produce toxic pollutants like polychlorinated dibenzodioxins and dibenzofurans (PCDD/F)<sup>1,2</sup>. Extreme soot and lower temperature in the exhaust gas in the duct right behind a wood incinerator requires an exact isokinetic sampling. Under these conditions an automatic sampling system was applied to investigate PCDD/F with instrumental analysis. Additionally a bioassay was established measuring the induction of CYP1A1-mediated ethoxyresorufin-O-deethylase (EROD) activity which comprises dioxins and dioxin-like compounds<sup>3</sup>. Furthermore the sampling train was extended to high volatile fractions of flue gas.

### Materials and Methods

#### Plant description and operating conditions:

Wood from house demolition was burned in a wood incinerator. The boiler of the incinerator has a nominal output of 120 kW and the recovered energy is used for house heating and warm water generation. The oven was subsequently fed until the boiler achieved a temperature of 80 °C. Twice a day the wood incinerator was fed in summer and several times a day in winter. The combustion chamber was fed manually with approximately 20 kg dry and humid old wood. The sampling time represents one combustion interval. The combustion interval corresponded to the amount of wood fed and type of the wood and lasted between one and two hours. The sampling started after feeding wood and was finished after burn out from the wood in the combustion chamber. The gas velocity in the duct of 25 cm diameter was between 2 and 7 m/s. The oxygen content was approximately 5 % (v/v) in the main burning period and increased to 20 % (v/v) at the end of the process. At the beginning of the process the incomplete combustion resulted in high concentrations of carbon monoxide and reached a content of more than 6000 mg/m<sup>3</sup>. The temperature varied between 220 and 280 °C. The sampling point was located at the side of a horizontal duct two meters behind the wood incinerator.

#### Sampling system:

The sampling system represents the automated version of the cooled probe method<sup>4,5,6</sup> and is depicted in Figure 1. The nozzle and the pressure head were positioned at equal pressure conditions in the duct. The nozzle was constructed from glass with a diameter of 15 mm and connected to a cooler. Thereby the sample gas was cooled to temperatures below 30 °C. Condensate was trapped in a flask.

Downstream, a battery of cartridges were linked to collect the soot particles and gaseous PCDD/F. The first cartridge was filled with glass-wool for trapping the PCDD/F which were adsorbed to the soot. On the bottom of the cartridge a glass fibre filter was fixed to retain fine particles. The second cartridge contains 50 g XAD-2 resin for adsorption of the gaseous PCDD/F. A second back-up XAD-2 cartridge is attached to control the breakthrough of PCDD/F. The following two u-shaped glass tubes were filled with 3 ml pentane to absorb volatile compounds. The tubes are embedded in a dry-ice bath which was kept at -70 °C. The sucking device was connected to this arrangement. The regulating unit was installed between the gas volume meter and the vacuum pump. The flow rate of about 1.5 to 2 m<sup>3</sup>/h was regulated by the control unit. The analytical procedures for the extraction of the cartridges, the clean up and the determination are described elsewhere <sup>7</sup>.

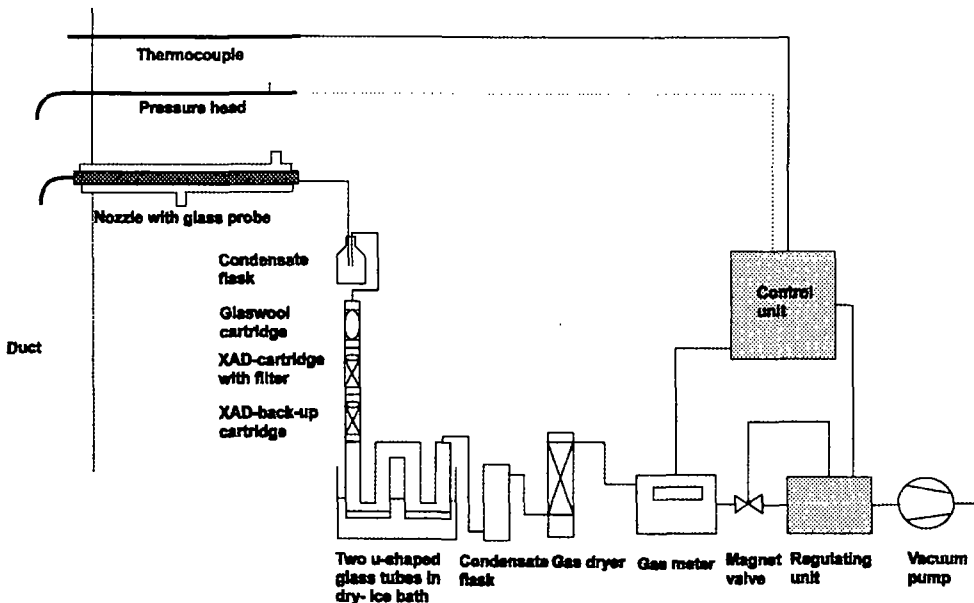


Figure 1: Sampling train for application of the cooled probe method using the automatic system and additional trapping units for volatile compounds.

The following quality assurance was carried out: The sampling train was thoroughly cleaned, the adsorbent used was supplied precleaned, the glass-wool was spiked with <sup>13</sup>C-labelled PCDD/F, a leak check was made before the sampling. A control blank was taken before each sampling campaign. The condensate was poured over the XAD-cartridge. In the filtrate no PCDD/F were found. The collection efficiency of the sampling train has been validated to at least 95 %. The sample gas flow rate was adjusted continuously and automatically by a regulating valve controlled by a microprocessor. All relevant physical data of the flue gas for the calculation of the desired sample gas flow rate were registered each minute. A calibration of the automatic system before every sampling was carried out. The registration of the standard sample gas volume of the automatic system was compared to the sample gas volume of the gas meter. It was ensured that isokinetic conditions maintained for each sampling <sup>8</sup>.

## Results and Discussion

The PCDD/F concentrations measured at the wood incinerator are in the range between 0.35 ng/m<sup>3</sup> I-TE and 5.7 ng/m<sup>3</sup> I-TE. The difference of the values are probably due to the constitution of the wood. We have two different types of wood compositions: 50 % treated wood pieces, 50 % treated boards and 50 % treated boards, 50 % treated beams. However, the application of untreated wood cannot be excluded for the combustion. No detailed information exist about the quality of the wood used. Results are shown in Table 1.

Table 1: Results and parameters of the sampling campaigns at a domestic wood incinerator.

date	06.03.97	25.06.97	20.10.97	21.10.97	23.10.97 a	23.10.97 b
charge	50 % treated wood pieces, 50 % treated boards	50 % treated wood pieces, 50 % treated boards	50 % treated wood pieces, 50 % treated boards	50 % treated boards, 50 % treated beams	50 % treated boards, 50 % treated beams	50 % treated boards, 50 % treated beams
combustion interval [h]	2	2	1.5	1.5	1.5	1.5
the type of sampling	automatic	automatic	automatic	automatic	automatic	automatic
sampling time [h:min]	2:00	1:38	1:15	1:23	1:24	1:33
standard sample volume [m <sup>3</sup> ]	2.6	2.5	2.1	2.2	2.1	2.4
T <sub>start</sub> [°C]	200	141	165	268	204	249
T <sub>maximum</sub> [°C]	215	254	284	273	259	249
T <sub>end</sub> [°C]	130	126	106	118	134	137
T <sub>mean</sub> [°C]	182	175	196	203	217	210
I-TE GC/MS [ng/m <sup>3</sup> ]	2.5	2.2	5.7	0.35	0.94	0.35

Table 2: Bioassay results from the sampling campaigns at a domestic wood incinerator.

date	06.03.97	25.06.97	20.10.97	21.10.97	23.10.97 a	23.10.97 b
I-TE Bioassay [ng/m <sup>3</sup> ]			10.4	3.2		
I-TE GC/MS [ng/m <sup>3</sup> ] first u-shaped glass tube			0.00021			
I-TE GC/MS [ng/m <sup>3</sup> ] second u-shaped glass tube			0.00046			
I-TE Bioassay [ng/m <sup>3</sup> ] first u-shaped glass tube					0.029	
I-TE Bioassay [ng/m <sup>3</sup> ] second u-shaped glass tube					0.017	

The temperature course of all campaigns were similar. All samples show a nearly similar homologue pattern of PCDD/F (Figure 2).



Figure 2: The homologue pattern of PCDD/F of a wood incinerator.

The breakthrough of PCDD/F was less than 2 %. The PCDD/F concentrations of the volatile compounds in the U-glasses were smaller than 0.0005 ng/m<sup>3</sup>. In all of the measurements, the PCDD/F concentrations exceeded the actual limit for facilities controlled by the German ordinance for large scale emissions. Biological I-TE values (Tab. 2) are higher than values derived from chemical analysis obtained from HRGC/HRMS (Tab. 1). The apparent mean deviation was a factor of 5 and may partly be due to the fact that the I-TE value calculated from chemical analysis includes only 17 PCDD/F congeners. The bioassay results comprise the biological response to compounds like polyhalogenated biphenylethers, naphthalenes, dibenzothiophenes and alkylated, brominated or mixed halogenated dibenzodioxins/furans, which also bind to the Ah-receptor. Volatile compounds with a dioxin-like response in the bioassay seem to be negligible.

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