# Experiences gained from the sampling of chlorine aromatics in the raw gas of waste incineration plants -Conclusions with regard to dedusting technology

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## 1.Introduction

It is only possible to counteract primary formation of PCDD/F e.g. by further developments of the combustion technology, and hence, to contribute to meeting the minimization requirements, when consistent and regular sampling and determination of Cl-organic compounds (PCDD/F, chlorophenols and chlorobenzenes) are carried out in the raw gas of waste incineration plants. Here, not only the absolute concentration levels are of interest. In addition, the solid-bound and gaseous fractions have to be known, as they decisively influence the selection and design of the downstream exhaust gas cleaning systems.

For the determination of the solid-borne fraction the fly ash is separated by means of a heated filter. The gaseous fraction is collected in a condenser/adsorber combination (or only in an adsorber) located downstream of the dust separator. Then, these sample fractions are analyzed separately.

It is not clear, how Cl-organic compounds behave at temperatures ranging from 150 to 250°C in a fly ash layer developing during filtration and passed by the raw gas of a waste incineration plant. The experiments described below are all aimed at settling this question. Important parameters investigated are the filter cake temperature and the composition of the fly ashes. On the basis of the results, the chemist may draw conclusions with regard to the correctness of sampling and of the determination of Cl-aromatics. The process engineer may expect to gather important findings for optimized operation of large-scale dust separators.

## 2. Experiments on the influence of the filter material

Prior to study the effect of fly ashes on the organic exhaust gas components during particle filtration, the influence of the filter material (PTFE and quartz fibre) applied had to be tested. The experiments were performed at 2 filter temperatures ($T_1$=160°C, $T_2$=240°C). In particular at high temperatures (T=240°C), PCDD/F concentrations were found to be much smaller for the quartz filter compared to the PTFE filter. The differences obtained for ΣPCDD (factor 4) exceeded those observed for ΣPCDF (factor 2). When using quartz filters ΣPCDD/F concentrations at 160°C were smaller by about 40% than the values obtained when using PTFE filters. Chlorophenols and chlorobenzenes are not affected by any of these filter materials. Therefore only PTFE filters were used for the investigations on the effect of the filter cake during sampling mentioned below.

## 3. Experiments covering the influence of fly ash on the filter

These experiments were aimed at investigating the influence both of the temperature and the composition of the filter cake on the concentration of the pollutants studied. Sampling was carried out in the raw gas downstream of the boiler of a large-scale domestic waste incineration plant by means of three separate sampling systems.

### 3.1. Experimental setup

The experimental setup of the three sampling systems is represented in Fig.1.

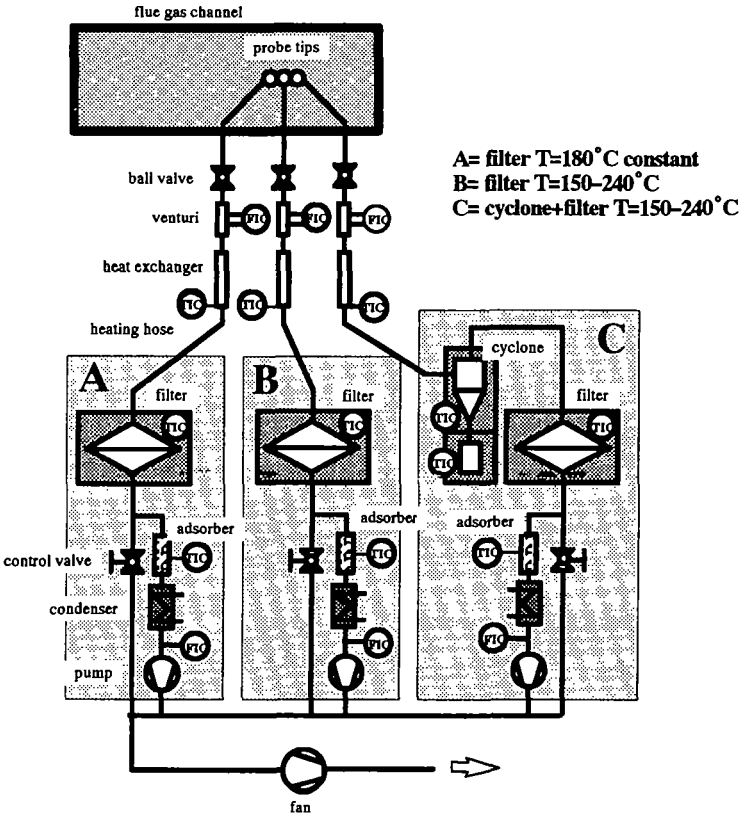


**Fig.1: Experimental setup**

Via identical probes, the exhaust gas was pumped separately for all three individual samplings. The three probe tips were arranged such that they were in contact with each other and, thus, their position was practically identical.

### 3.2. Test conduct

Sampling A served as the reference sampling. Sampling parameters were kept constant in all experiments. The gas and separation temperatures in the filter module always amounted to 180°C.

In the samplings B and C , the gas supply temperature downstream of the heat exchanger and the temperature in the respective dust separators were varied in the range of 150 to 240°C. All experiments were performed under constant conditions for a period of three hours.

## 4. Measurement results

### 4.1 Dust concentrations and inorganic dust constituents

By the determination of the dust concentration of the exhaust gas together with the inorganic analysis of the fly ash constituents, comparability of the individual samplings could be demonstrated. The concentrations of certain filter dust components measured during sampling C with a measuring cyclone being installed upstream of the filter stage as preliminary separator, sometimes considerably differed from the measurements during direct filtration ( sampling B). This can be attributed to the characteristic element enrichment in single size fractions.

### 4.2. Cl aromatics - raw gas concentrations

The Cl organic compounds studied did not exhibit any significant fluctuations of concentration of reference measurement A under constant sampling conditions over the duration of the experiments.

For all compounds the major fraction was obtained in the gas phase when differentiating between filter-passing and solid-adsorbed fractions under constant sampling conditions ( reference sampling A).

Up to about 200°C the results of B and C are identical with the reference measurement A . Above 200°C the concentration of all components investigated increased in both cases. The major fraction was also found in the gas phase.

## 5. Comparison of samplings

### 5.1. Comparison of samplings B and A ( filter/reference filter)

Samplings A (reference filter, T=180 °C ) and B ( filtration with temperature variation) are compared in Fig.2 for the integral parameters of the four classes of compounds studied. The

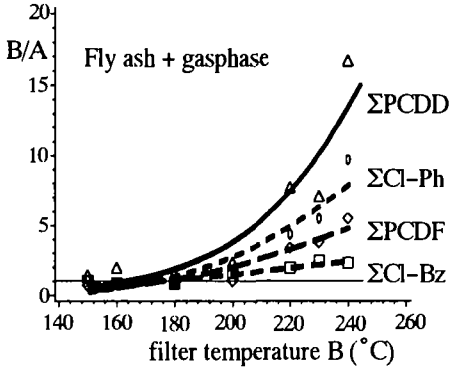


**Fig.2: Comparison of samplings B/A**

B/A ratios exhibit a partially exponential increase for all substances above a filtration temperature of about 200°C. This increase is strongest for PCDD and smallest for chlorobenzenes. These significant increases in concentration with increasing filter temperature can only be explained by a formation. Probably, PCDD formation takes place via chlorophenols, as described in references [1-4] . This, however, still remains to be confirmed. Below about 200°C, the calculated values are found to lie within the sampling and analysis error limits for B/A at

≈1. Contrary to previous findings [5-7], the formation temperature of the Cl organic substances investigated is much smaller.

## 5.2. Comparison of samplings B and C ( filter/cyclone+filter)

The integral parameters of the samplings B (filter) and C ( cyclone+filter) are represented in Fig.3 for the integral concentrations ( gaseous+dust-bound) as quotients B/C). Within the lim-

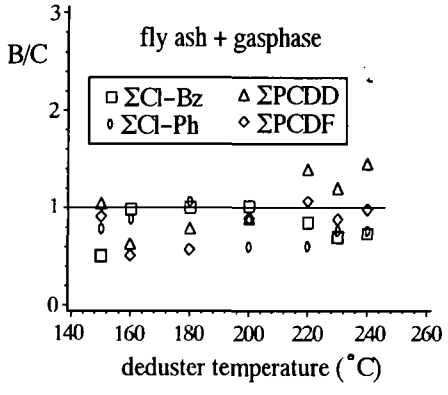


**Fig.3: Comparison of samplings B/C**

its of measurements accuracy, all Cl aromatics studied exhibit a nearly constant behavior as a function of the dust separation temperature, that means they are not affected by the measuring cyclone installed upstream in sampling C.

The fact that the formation of all Cl aromatics studied in the temperature range of 200-240°C is not influenced by a coarse-grain separation and the resulting reduction of the carbon content of the filter cake must be taken into account when investigating the mechanism of the formation reaction. Having a closer look at the TOC values of filter dusts in sampling C, it can be noted that they decrease from about 30 mg/g at the low temperature to about 10 mg/g at the higher temperatures. Hence an oxichlorination of the carbon might be the cause for this formation.

## 6.Conclusions with regard to dedusting technology

The results obtained from raw gas sampling of Cl aromatics as a function of temperature are of crucial importance for the design and operation of dedusting systems.

For the first time the results demonstrate in an unambiguous manner that 200°C represents a critical threshold temperature for dust separation with bag filters. Above this temperature, significant formation of Cl aromatics and in particular of PCDD and chlorophenols as well as of PCDF takes place.

As far as the use of electrical precipitators is concerned, it was demonstrated by a balancing experiment carried out a few years ago using a two-field electrical precipitator in the temperature range of 215-250°C [8,9] that formation of PCDD/F occurs. The formation factors of PCDD were found to exceed those of PCDF by about a factor of 3. This preferential formation of PCDD compared to PCDF in the range from 200 to 250°C is in agreement with the results obtained in the present work and suggests a comparable formation mechanism. It still remains to be found out, wether electrical precipitators and fabric filters also have a threshold temperature of 200°C for formation. Due to the results presented here, however, this seems to be very probable.

## 7. References


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