Influence of Ozone on Chlorophenol, Chlorobenzene and PCDD/F Sampling in the Exhaust Gas of a Waste Incineration Plant

S. Kreisz, H. Hunsinger, H. Seifert
Karlsruhe Research Center
Institute for Technical Chemistry, Thermal Waste Treatment Division
D–76021 Karlsruhe, P.O. Box 3640, Germany

1. Introduction

Various sampling techniques were applied for studying the influence of filtration systems in waste incineration plants on the concentration of chlorinated aromatic compounds in the exhaust gas. Principle suitability and comparability of the results had been demonstrated for various sampling trains 1).

It was therefore rather surprising to find that the PCDD/F concentrations varied considerably depending on the sampling technique applied in some (not all) experiments performed downstream of the ESP in the exhaust gas of a waste incineration plant. The same effect, but in a less intensive form, could be observed for chlorobenzenes and chlorophenols. Comparative measurements in a plant downstream of the fabric filter did not yield such a result.

Knowing that the PCDD/F concentration can be reduced by the injection of ozone into the raw gas 2) and that ozone may be produced by electrofilters, it was decided to investigate the influence of ozone under defined boundary conditions in a bypass system of our TAMARA waste incineration test plant 3).

2. Experimental

To obtain data on all sampling trains which are usually applied, the condensation method (condensation+downstream adsorber) and the direct adsorption method (adsorber+downstream condensation) were studied. In addition, two different adsorbers (lignite carbon (HOK) and XAD–2) were tested. The experimental setup is represented schematically in Fig. 1.

Following the addition of a defined amount of ozone, the dust–free exhaust gas passed a static mixer and the sampling trains B–E arranged in parallel. Prior to the addition of ozone, input measurement A was performed.

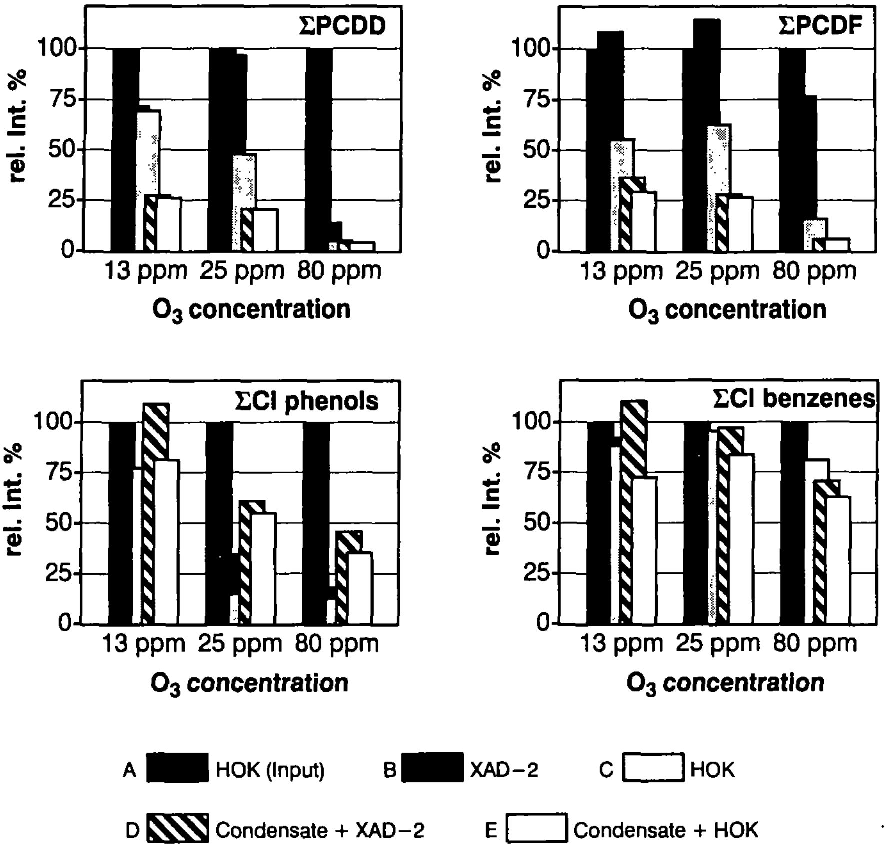

Fig.2: Relative intensity of the integral values of the chloroorganic compounds in the different sampling trains depending on the O_3 concentration

Direct adsorption method: When using this method, PCDD/F reduction is always smaller than in the condensation method. However, it is found to be dependent on the adsorber applied. While a lignite carbon adsorber shows a strong tendency towards smaller PCDD/F values at 13 ppm O_3 already, the input values are still reached at 25 ppm O_3 when using XAD-2. At 80 ppm O_3, however, also XAD-2 exhibits a PCDD/F reduction of >80%. As compared to the condensation method, chlorophenol concentration is much more reduced. Without an upstream condenser, ozone settles on the adsorber surface and may destroy the adsorbed chlorophenols. It must be noted that the concentration of chlorobenzenes is practically identical to the values obtained when using the condensation method. Obviously, the chlorobenzenes are stable to oxidation under the conditions prevailing during sampling.

4. Conclusions

The following conclusions may be drawn with regard to the sampling of chloro-organic compounds in ozone-containing exhaust gases:

- Stability to ozone decreases in the order of chlorobenzenes>chlorophenols>PCDF>PCDD.

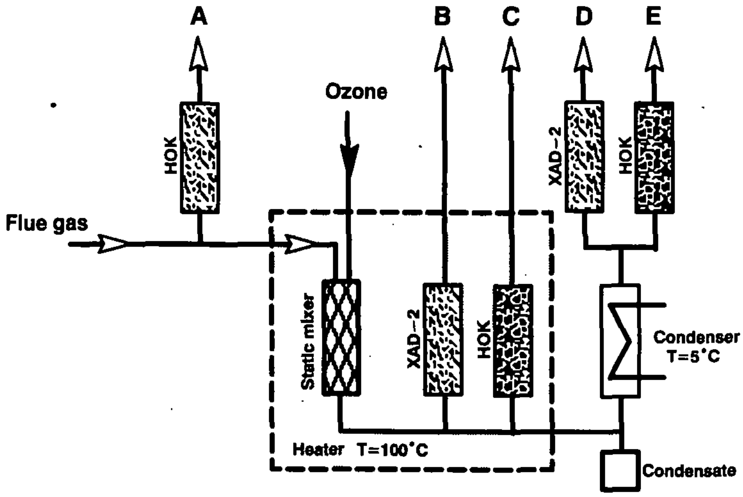

Fig. 1: Schematical flow sheet of the measurement configuration

The ozone was generated by a laboratory ozonizer in an oxygen flow (0.1 Nm^3/h). Ozone concentration was determined prior to and upon the completion of each experiment by means of titration according to DIN 19627 [4]. The flow rate of all sampling trains amounted to 0.5 Nm^3/h and was controlled by means of mass flow controllers. The duration of the experiments was 7h each. The experiments were repeated several times. The samples were then analyzed for chlorobenzenes, chlorophenols and PCDD/F.

3. Results

Preliminary tests without ozone addition in the sampling trains A–E yielded identical values within the error limit. The experimental results obtained for various sampling trains are represented graphically in Fig. 2 as a function of ozone concentration in the exhaust gas.

Condensation method: At O_3 concentrations of 13 ppm already, PCDD/F reductions of about 75% occur. At 80 ppm O_3 in the exhaust gas, <5% of the PCDD/F input value is measured. Concentration of chlorobenzenes is less affected by ozone than PCDD/F concentration. At low ozone concentration, chlorobenzene concentration remains unchanged and even at a concentration of 80 ppm O_3 a slight reduction can be noticed only. The various decomposition rates can be explained by the varying separation efficiencies of the individual substances in the condensate. While a large fraction of PCDD/F (>90%) is separated in the condensate, nearly all chlorobenzenes (>95%) penetrate into the condenser. Under the experimental boundary conditions, separation efficiency of chlorophenols in the condensate is about 60–70%. As the ozone contained in the exhaust gas is almost completely dissolved in water, the compounds separated on the downstream adsorber cannot be attacked by ozone, while the molecules dissolved in water undergo decomposition.

- Under these conditions, the condensation method is not suited for the determination of the PCDD/F concentration in the exhaust gas.
- At ozone concentrations of <25 ppm, direct adsorption on XAD–2 is the method of choice.
- At high ozone concentrations (>25 ppm), correct sampling with one of the sampling trains studied is impossible.

5. References

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