Simultaneous Sampling of Polychlorinated and Polycyclic Aromatic Compounds Upstream and Downstream of the Boiler of the Karlsruhe Test Incinerator TAMARA

Thomas Wanke, Jürgen Vehlow, Institut für Technische Chemie, Bereich Thermische Abfallbehandlung, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany
Klaus Jay, Institut für Technische Chemie, Bereich Chemisch-Physikalische Verfahren, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany

Introduction

During the last decade a great number of organic compounds, preferentially halogenated ones, has been analysed in the flue gas of municipal solid waste incinerators (MSWI) [1),2)]. A major concern was to evaluate the formation mechanisms of these mostly harmful pollutants. Most of the measurements were performed in the temperature range around or below 200 °C. From theoretical considerations and laboratory scale experiments formation mechanisms have been proposed which could be confirmed to a great extent by correlating specific operation parameters and the respective concentration level in the flue gas. A different approach to establishing formation routes is the simultaneous analysis of the flue gas composition at different locations along its way from high temperatures in the combustion chamber down to the 200 °C level at the back end of the boiler [3),4),6)]

The following report describes results of simultaneous gas sampling directly in front and downstream of the boiler of the Karlsruhe test incinerator TAMARA. The samples were analysed for polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), benzenes (PCBzs), phenols (PCPhs), and biphenyls (PCBs) as well as for polycyclic aromatic hydrocarbons (PAHs).

Experimental

The test incinerator TAMARA is a mass burner with a nominal throughput of 200 kg/h of pretreated and homogenised household waste. The schematic of the furnace is given in **Fig. 1**.The furnace is equipped with a 4-zone feed grate. The residence time on the grate is approximately 30 min. The design of the combustion chamber can be changed by means of a mobile roof between counter current and parallel flow geometry. The latter one, shown in **Fig. 1**, has been used during the experiments

described below. The flue gas leaves the combustion chamber at typical temperatures of 900 °C. It passes the gas ducts and the boiler within approximately 10 s being cooled down on the way to 180-200 °C. The first sampling was performed at location 1 in **Fig. 1**. The flue gas had an averaged temperature of approximately 700 °C at this position. The sample was taken by means of a water-cooled probe comprising a ceramic tube of 7 mm i.d. and an outer steel tube for the cooling water. The gas leaves the 1 m long probe at a temperature of 30 °C and is then directed to a cooling device where it is cooled down to 5 °C. After this condensation step the gas passes a XAD-16 bed for adsorption of organics. Condensates and XAD were analysed. The second sampling took place downstream of the boiler at a gas temperature of 200 °C using the isokinetic long-time sampling train described in detail in [5]. In this case the fly ashes, the condensates and adsorber had to be analysed.

The sampling periods were 4 h each and the gas volume always 3-4 m^3. The clean-up and measurements are described in [6].

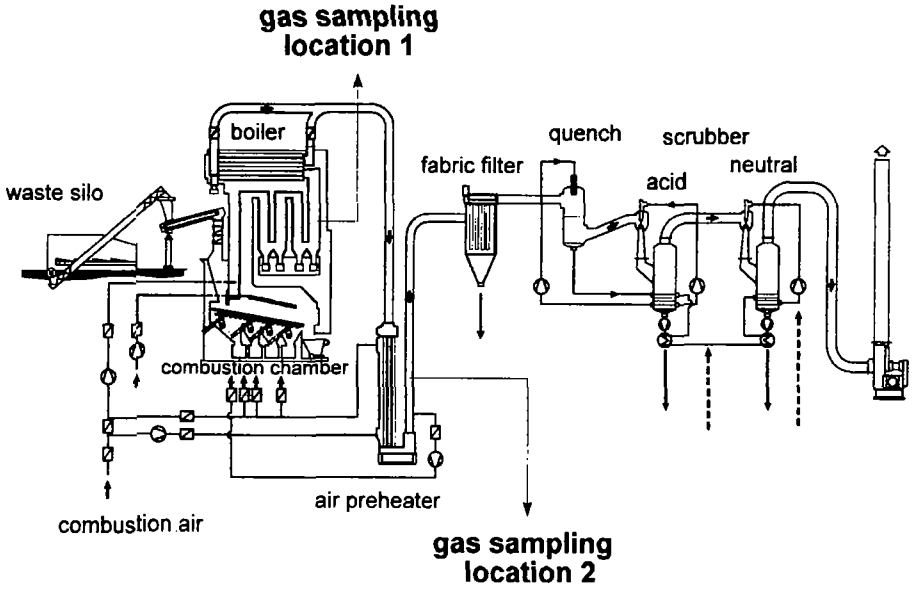

Fig. 1 Schematic drawing of the test incinerator TAMARA

Discussion of Results

Fig. 2. compiles the results of the compound classes achieved during 10 experiments. It is well known that the different classes of compounds establish different concentration levels in the flue gas of a MSWI. The sum of homologues downstream of the boiler of PCDDs as well as of PCDFs scattered between 20-40 ng/Nm^3. Sum concentrations of PCBs were found to be slightly higher with 50-100 ng/Nm^3. According to data found in literature the PCBzs and PCPhs were exceeding these levels

by 1 to 2 orders of magnitude. The sum concentration of 13 selected PAH was about 0.2-2 µg/Nm^3 being characterised by a distinctive scattering.

Not only the concentration levels differed but also the relation of concentrations analysed at high to those measured at low temperature reveals a different fate of different compounds when passing the boiler. The graphs in **Fig. 2** indicate two types of classes of compounds characterised by

- increased concentrations inside the boiler, caused by a formation reaction (PCDD/Fs, PCBzs and PCPhs) or
- more or less decreasing levels caused by (thermal) destruction (PCBs and PAHs).

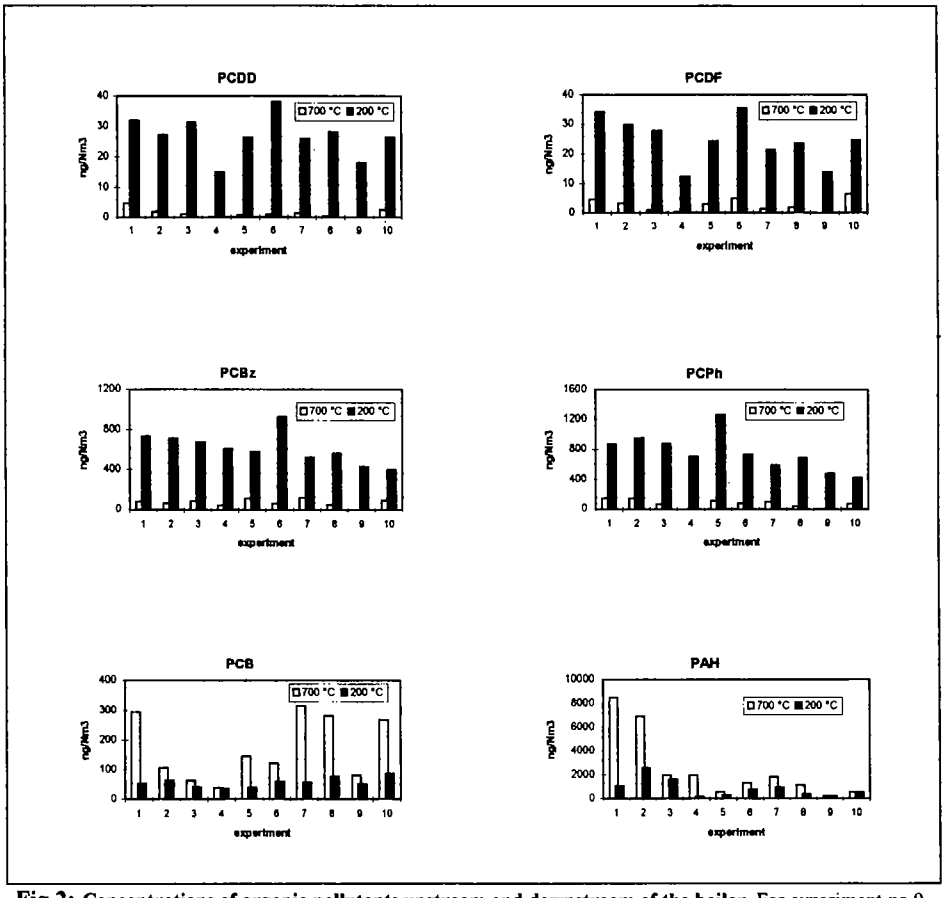

Fig 2: Concentrations of organic pollutants upstream and downstream of the boiler. For experiment no.9, the values measured for PCDDs, PCDFs, PCBzs, and PCPhs upstream of the boiler are not indicated.

The findings for PCDD/Fs, PCBzs and PCPhs are supported by published results *from sampling in full scale* incineration plants [3)4)6)]. In samples taken from flue gas at high temperature very low levels of PCDD/Fs are reported. In our campaign the

PCDD/Fs concentrations upstream of the boiler were often < 1 ng/Nm^3. This result is in agreement with the generally acknowledged de novo synthesis taking place as an oxichlorination of particulate carbon in the boiler in the temperature range between 550 and 200 °C [7]. A similar de novo synthesis is proposed for the PCBzs and PCPhs which is supported by our findings, too [8].

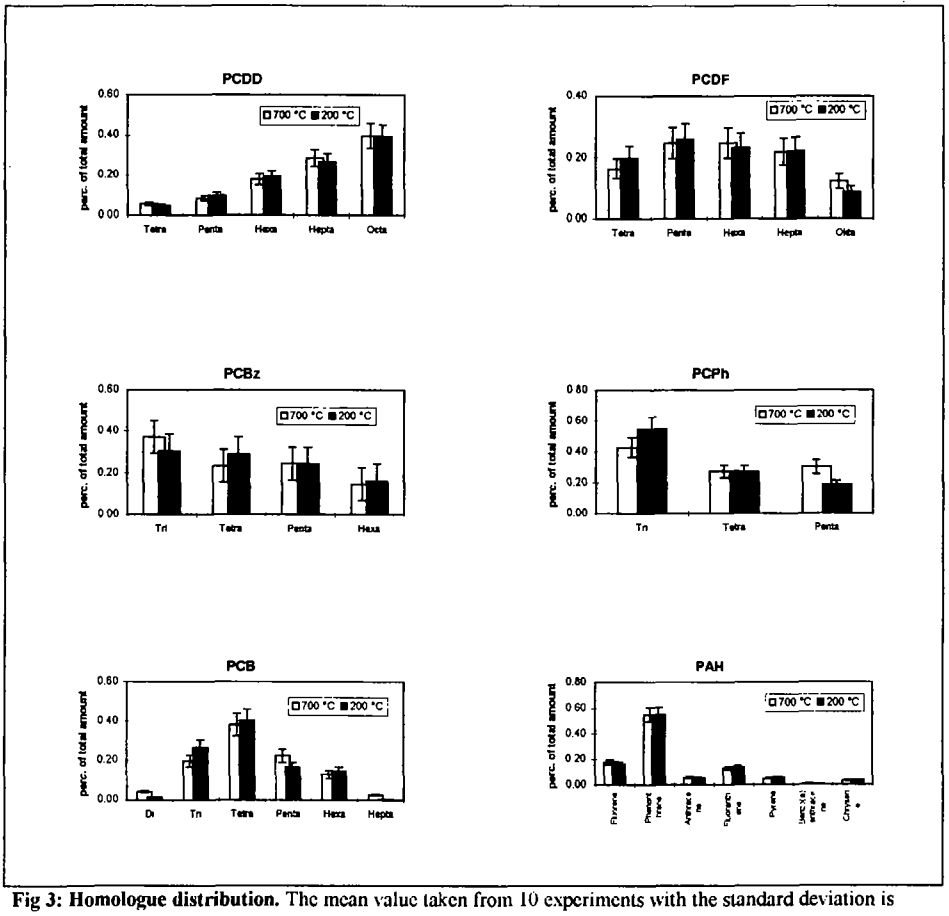

Fig 3: Homologue distribution. The mean value taken from 10 experiments with the standard deviation is represented.

In view of the de novo theory the low amounts of halogenated compounds detected at 700 °C might be an artefact caused by the same formation route inside the sampling train since we were not able to perform a real shock cooling within fractions of seconds.

An indication of such artefacts may be deduced from the homologue pattern of the respective compounds seen in **Fig. 3**. In laboratory experiments different homologue pattern have been obtained for PCDDs and PCDFs synthesised at different temperatures [9]. The constant homologue pattern found at high and low temperature in our

experiments is most easily explained if the same formation mechanism is assumed to take place inside of the sampling train as well as inside the boiler.

The laboratory experiments in [8] claim a de novo synthesis for PCBs, too. This is not in line with our experimental results since the PCB levels in TAMARA were equal or in most cases by a factor up to 5 higher at high temperature than they were at low temperature. The same behaviour is detectable for PAHs. The concentration factor between both of the sampling positions scattered substantially, whereas the homologue pattern stayed constant. There are two possible explanations for this behaviour:

- The formation of PCBs and PAHs starts already at very high temperatures and is completed at 700 °C. On the way down to temperatures of 200 °C thermal destruction is prevailing.
- In the MSWI formation of PCBs and PAHs is mainly following a fast gas phase reaction at high temperatures. In this case the formation should be similar in the sampling train as it is in the boiler. However, the longer residence time at temperatures between 700 and 200 °C in the boiler leads to higher thermal destruction.

On the basis of the achieved results no preference can be given. Especially tailored experiments in TAMARA with sampling at other positions and changes in the temperature field have already been designed to verify one or the other formation route.

Conclusions

- It has been demonstrated by the domestic waste incineration experiments in the TAMARA test facility that PCDDs, PCDFs, PCBzs and PCPhs hardly exist in the raw gas upstream of the boiler at 700 °C and are generated above all inside the boiler.
- The raw gas levels of PCBs and PAHs decrease between inlet and outlet of the boiler. The formation reactions for both of these species in full scale MSWIs do not follow those found in laboratory in a satisfying way. Due to our experiments, however, thermal destruction prevails in the temperature range of 700 to 200 °C.
- The real extent of de novo in the case of PCDD/Fs, PCBzs and PCPhs and of destruction in the case of PCBs and PAHs cannot be quantified due to possible artefacts at the high temperature sampling train.

References

(1) National Incinerator Testing and Evaluation Program: Environmental Characterization of Mass Burning Incinerator Technology at Quebec City
Report EPS 3/UP/5, June 1988

(2) Fängmark, I., van Bavel, B., Marklund, S., Strömberg, B., Berge, N. and Rappe, C.
Influence of Combustion Parameters on the Formation of Polychlorinated Dipenzo-p-Dioxins, Dibenzofurans, Benzenes, and Biphenyls and Polyaromatic Hydrocarbons in a Pilot Incinerator
Environ. Sci. Technol. (1993) 27, 1602-1610

(3) Düwel, U., Nottrodt, A., Ballschmiter, K.

Simultaneous sampling of PCDD/PCDF inside the combustion chamber and on four boiler levels of a waste incineration plant
Chemosphere, (1990) *20, 1839-1846*

(4) Benfenati, E., Mariani, G., Fanelli, R., Zuccotti, S.
"De Novo" Synthesis of PCDD, PCDF, PCB, PCN and PAH in a Pilot Incinerator
Chemosphere (1991), *22*, 1045-1052

(5) Vogg, H., Merz, A., Becker, E.
Permanent monitoring of the emission of highly ecotoxic substances from waste incineration plants
Proceedings of the 1991 Incineration Conference, Knoxville, Tn, May, 1991, 555

(6) Mariani, G., Benfenati, E., Fanelli, R.
Concentrations of PCDD and PCDF in different points of a modern refuse incinerator
Chemosphere, (1990) *21*, 507-517

(7) Vogg, H., Stieglitz, L.
Thermal behaviour of PCDD/PCDF in fly ash from municipal incinerators
Chemosphere, (1986) *15*, 1373-1378

(8) Stieglitz, L., Zwick, G., Beck, J., Bautz, H., Roth, W.
Carbonaceous Particles in Fly Ash- a Source for the De-Novo-Synthesis of Organochlorocompounds
Chemosphere, (1989) *19*, 283-290

(9) Schwarz, G.
Bildung und Verhalten von organischen Spurenstoffen auf Flugaschen der Müllverbrennung
Dissertation (1991) Universität Heidelberg