

## Time – an underestimated factor concerning correlations of halogenated organic compounds and combustion conditions in MSWI

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Municipal solid waste (MSW) is a very inhomogeneous fuel, which varies widely in its chemical composition and physical properties. At modern waste incineration plants (mainly grate systems) fluctuations of the heating value can almost be compensated by controlling the feed rate, the grate kinematics and the air supply in order to guaranty an effective carbon burnout of the bottom ash and of the flue gas. At controlled combustion conditions the concentrations of PCDD/F in front of the flue gas cleaning system of modern facilities range from 1-2 ng TEQ/Nm<sup>3</sup>. However, during and after disturbed combustion conditions (e.g. start-up, shut down or operational failures)<sup>1-4</sup> the PCDD/F raw gas level can increase by one or two orders of magnitude. Therefore efficient flue gas cleaning by catalytic or adsorptive processes is needed to guaranty permanently stack emissions below 0.1 ng TEQ /Nm<sup>3</sup>.

To improve the economy of combustion processes by suppressing the formation of pollutants already at their source and reduced efforts in flue gas cleaning are of major concern. For example NO<sub>x</sub> minimization by staged combustion and stoichiometric dosage of reducing agents in SCR or SNCR processes is an established technology. The basis of such control strategies requires always real-time measurements of the respective pollutants.

Compared to NO<sub>x</sub> the situation for PCDD/F is much more complicated. PCDD/F comprises a large number of isomers each valued with a specific toxic equivalent factor. Regarding the emission limit value of 0.1 ng TEQ/Nm<sup>3</sup>, monitoring would require extremely low detection limits for each individual toxic isomer. Additionally in flue gases loaded with fly ash PCDD/F can be partly adsorbed on the ash particles depending on their carbon content. Therefore PCDD/F cannot be measured online. Accurate detection of PCDD/F still needs expensive sampling methods comprising fly ash filtration and adsorption methods over a relatively long period of time (usually >1h) followed by offline GC/MS analysis. To overcome the lack of real-time PCDD/F measuring methods it has been proposed to monitor low chlorinated chlorobenzenes, chlorophenoles or even one single low chlorinated dioxins/furan isomer which can be measured online in the gas phase by modern methods<sup>5-7</sup> like REMPI-TOFMS. Many studies based on conventional sampling methods showed reasonable correlations of these compounds with PCDD/F TEQ data (average concentrations over long sampling time)<sup>8-12</sup>. But this precondition alone is not sufficient regarding an online process characterization and control. Measured data must also reflect the actual situation of the combustion process in real time.

Therefore an experimental program was carried out at our test plant TAMARA in order to generate reliable data concerning the time scale of the formation of individual halogenated organic compounds in the flue gas downstream of the boiler in order to detect effects of short term changes in fuel composition as well as in combustion conditions.

The following investigations were based on the idea to use bromine as a tracer in the formation of halogenated organic compounds. Bromine and chlorine have a quite similar behaviour in de-novo synthesis<sup>13, 14</sup> which is supposed to be the major formation mechanism of halogenated dioxins und furans in municipal solid waste incineration plants equipped with a boiler for heat recovery.

### Experimental

Experiments were carried out at our pilot waste incinerator TAMARA (waste capacity = 200 kg/h). Details of the plant are described elsewhere<sup>4</sup>. The plant is equipped with complex online monitoring devices for all process relevant parameters and can be operated under well defined conditions by using defined waste compositions and a universally applicable process control system.

The experiments described here were part of a program of transient combustion conditions. Sampling of halogenated

organic compounds as well as of special inorganic gases and fly ashes took place at the end of a 3 week campaign during 4 days in subsequent time intervals in the raw gas downstream of the boiler.

The investigations were started by a reference sampling (1), where municipal solid waste (MSW) with a very high Cl/Br ratio of about 100 was burnt. Afterwards the fuel quality was changed by co-feeding of electronic scrap (mainly flame retarded plastics) with high bromine concentrations. This fuel mixture was kept constant for about 48h. Then the fuel was changed back to reference quality. Sampling was continued for another 24h.

This basic program included additional special conditions which are schematically summarized in Fig. 1 including the sampling periods of halogenated organic compounds. At sampling (4) a not planned operational failure caused by piling up fuel in front of the grate occurred. To investigate the so-called "Griffin reaction"  $^{15}(\text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2 \text{HBr})$  the sulphur content of the fuel was increased by adding elemental sulphur to the fuel during sampling (13). The boiler deposits were removed by a mechanical cleaning device at defined time intervals. The data of all experimental conditions are necessary to get a deeper insight in the complex process of the formation of halogenated organic compounds in a real MSWI and especially about correlations between the individual compounds as well as the relevance of actual combustion conditions and fuel composition.

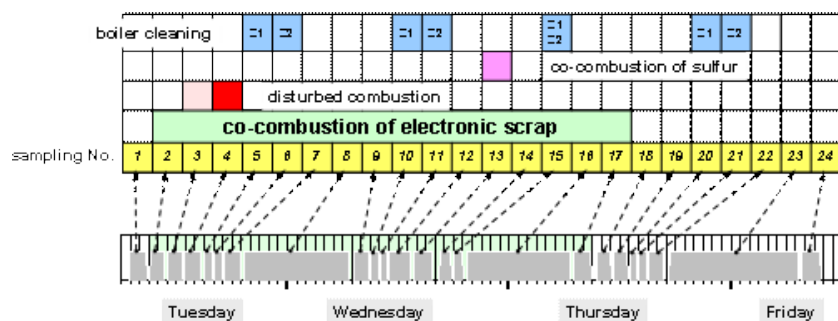


Fig. 1: Time scale of experiments and sampling intervals

Sampling of halogenated organic compounds<sup>16</sup> was carried out in the raw gas downstream of the boiler at temperatures of about 200°C. The samples were analyzed for the homologues of pure chlorinated, pure brominated and mixed halogenated organic compounds: benzenes (number of halogenation X=2-6), phenols (X=2-5) and dioxins/furans (X=4-8) by GC/MS.

## Results

After reference sampling the fuel composition was changed immediately in one step, kept constant for 48h and then switched back again to reference fuel. The time interval when co-combusting electronic scrap (with high bromine content) was characterized by a significantly increased level of inorganic bromine species ( $\text{HBr} + \text{Br}_2$ ) up to 400  $\text{mg}/\text{Nm}^3$  in the flue gas. Fig. 2 shows the respective ratios of Cl/Br of the flue gas and the fly ash composition over the total experimental duration.

Parallel to the total bromine concentration Cu in the fly ash was increased by a factor of about 5 up to 20 $\text{mg}/\text{g}$ . The concentration of  $\text{SO}_2$  showed a decrease during burning electronic scrap while  $\text{SO}_3$  was increased adequately. According to "Griffin reaction" this finding indicates that high levels of  $\text{Br}_2$  (up to 250  $\text{mg}/\text{Nm}^3$ ) were present in the flue gas.

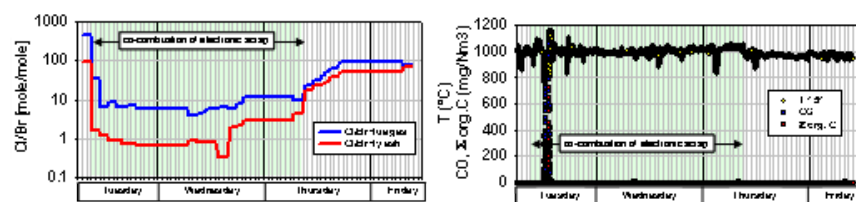


Fig. 2: a) Cl/Br ratios of the flue gas and the fly ash, b) disturbed combustion

At the end of sampling (3) the fuel flow accumulated just in front of the grate. As consequence the excess of combustion air caused decreasing combustion temperatures and increased CO levels. During sampling (4) the deposited fuel was moved on again (4) and caused combustion conditions at oxygen deficiency. The temperature at the exit of the combustion chamber rose up to almost 1200°C and very high concentrations of CO (above metering range of 1000mg/Nm<sup>3</sup>), hydrocarbons (CH<sub>4</sub>) as well as soot particles (30 mg C/g fly ash) were detected in the flue gas. To avoid a long term “memory effect” of dioxin formation from the soot contaminated boiler deposits the boiler was subsequently cleaned by a mechanical cleaning device (sampling 5, 6). Further boiler cleaning procedures were carried out at sampling no. 10, 11 and 15 and 20, 21.

In Fig. 3 the relative distribution of pure chlorinated, pure brominated and themixed halogenated compounds of dioxins/furans, benzenes and phenols are depicted as function of time. Pure brominated compounds for dioxins and furans were not detected at halogenation degrees of 4 to 8. In contrary the halogenated benzenes and especially the phenols showed significant amounts also for pure brominated species, preferentially at low halogen degrees.

Comparing the plots with the Cl/Br ratios of inorganic species in the flue gas and in the fly ashes it is obvious that even after 4 hours of burning electronic scrap nearly no increase of the fraction of Br containing species of dioxins and furans could be observed. The more volatile compound of halogenated benzenes and especially of halogenated phenols were found to be much more sensitive to indicate changes of the Cl/Br ratio.

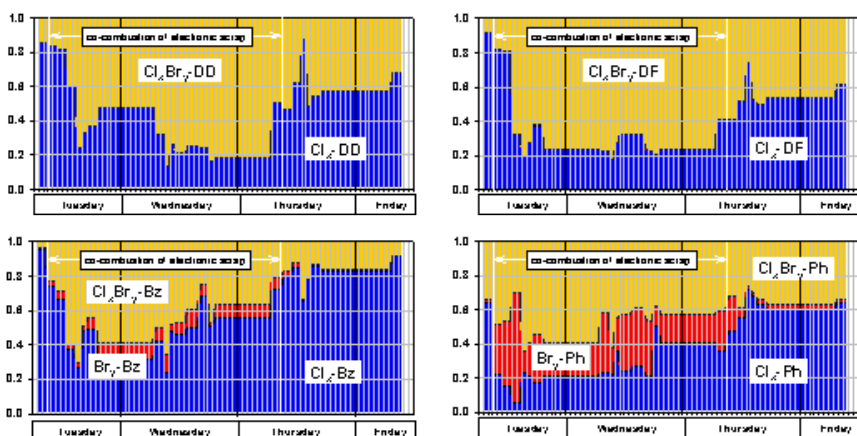


Fig. 3: Distribution of pure chlorinated, pure brominated and mixed halogenated organic compound during the whole experimental program.

Immediately after the operational upset (sampling 4) also for dioxins/furans and benzenes significant fractions of mixed halogenated species were detected. This situation continued further on with time on a consolidated level during the boiler cleaning intervals (5, 6) and the remaining co-combustion interval. Switching back to the standard fuel with low bromine content the fraction of bromine containing organic compounds showed a slow decrease back to the reference situation. While the low volatile benzenes and especially the phenols reach the reference distribution after some hours, the dioxins and furans were even after 24 h still away from the original distribution of sampling (1).

The absolute concentrations during the experimental program shown in Fig. 4 reveal that very high concentrations of all compounds could be detected during the failure condition (4) but also during all boiler cleaning procedures (5, 6 and 10, 11 and 15 and 20, 21) despite of actually excellent combustion conditions.

The short term increase of SO<sub>2</sub> (about 2h) by co-combusting elemental sulfur (13) had no effect on the formation rate of halogenated organic compounds despite the significantly lowered level of Cl and Br in the fly ash. These results agree well with the earlier findings<sup>17</sup> that only permanent high SO<sub>2</sub> concentrations lead after a long time (some days) to sulfate rich and halogen low concentrations of the ash deposits and in consequence to low formation rates of PCDD/F. This indicates once more that the dominant formation reaction of PCDD/F is caused by de-novo synthesis

from ash deposits in the boiler section.

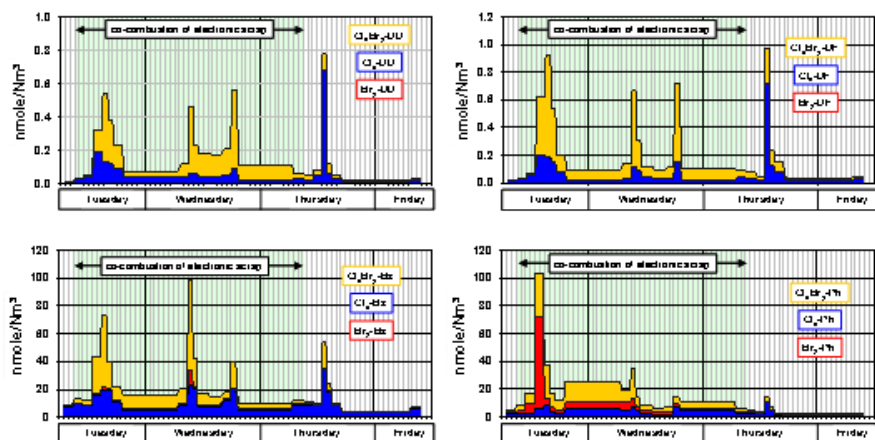


Fig. 4: Absolute concentrations of halogenated organic compounds in the raw gas

## Discussion

All data show that the concentrations of halogenated dioxins/furans, benzenes and to a lower extent of the phenols are not suited to reflect the actual combustion situation (boiler cleaning) and also not the fuel quality (Cl/Br ratio). Formation of these compounds occurs dominantly by de-novo synthesis inside the fly ash deposits. The kinetic of this formation mechanism is rather slow and the subsequent release to the flue gas by diffusion through the pores of the ash layer is also a very slow process, depending on the molecular weight of the individual compound. This behavior is confirmed by a shift of the homologue profiles to the higher halogenated compounds during boiler cleaning as well as the more sensitive Cl/Br ratio of low halogenated compounds to actual conditions. The very high amounts of the halogenated compounds released to the flue gas during boiler cleaning must be concentrated in the very small gas volume of the pores between the deposited ash particles or might also partly be adsorbed on the ash surface. In summary the transport of halogenated organic compounds from the interior of the ash deposit to the flue gas resembles a kind of chromatography. This finding might explain why higher chlorinated benzenes (Cl<sub>5</sub>Bz, or Cl<sub>6</sub>Bz) and phenols (Cl<sub>5</sub>Ph) with more similar physical properties compared to PCDD/F result in better correlations with the PCDD/F TEQ than the respective low chlorinated ones.

## Conclusions

Measured concentrations of halogenated organic compounds downstream a boiler of MSWI are the result of "individual memory effects" integrating the history of the fuel quality as well as the combustion conditions over many hours. Therefore it is proposed that real-time data of halogenated organic compounds downstream of the boiler are not suited as parameter for real-time combustion control in MSWI equipped with a boiler for heat recovery.

When correlating the concentration data of different species of halogenated organic compounds and also when using correlations between low and high halogenated homologues of the same compound class the individual physical properties must be taken into consideration.

## References

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