On-line PCDD/PCDF and PCDD/PCDF surrogate monitoring – basic difficulties due to formation characteristics, memory effects and removal efficiency of air pollution control devices

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Introduction

Establishing systems for on-line measurement of PCDD/PCDF or PCDD/PCDF surrogates has proved to present numerous challenges over the past 15 years. In recent years, considerable progress has been achieved with on-line measurement systems itself and some techniques have the technical requirements to detect TEQ relevant higher chlorinated PCDD/PCDF.

The key challenge of establishing such systems remains whether the objectives of on-line monitoring can be achieved. One ambitious aim of on-line emission monitoring is the measurement of stack gas for compliance with regulation limits. Another intended goal is the process control of an incinerator for reduction of PCDD/PCDF emission. A further, more realistic, approach is the monitoring of surrogates for general evaluation of emission characteristics, the supervision of air pollution control devices (APCDs) and for investigation of certain processes in the post combustion section and the APCDs.

Several indicator compounds were proposed for an estimation of PCDD/PCDF/PCB (TEQ) emission from incinerators. These include for example chlorobenzenes[1-4], chlorophenols[2,5], lower chlorinated PCDD/PCDF[2,6] or sum-parameters like semi- and non-volatile organohalogen compounds[3,4]. However, despite a basic correlation of e.g. TEQ and P_5CBz concentration (one of the most promising surrogates), the ratio between the surrogate and TEQ can vary one order of magnitude within the same incinerator and nearly two orders of magnitude when comparing different incinerators[1,3]. This demonstrated that a “simple” correlation of surrogates and PCDD/PCDFs can not be established, but that the understanding of the relationship of surrogates and PCDD/PCDF require a better understanding with respect to their behaviour within an incinerator.

The present paper discusses possible causes for the differences of the ratio of PCDD/PCDF (TEQ) and surrogates in incinerator flue gases and their implications for on-line measurement in system control and compliance monitoring.

Discussion

1) Correlation of PCDD/PCDF and surrogates based on formation pathway

PCDD/PCDF and surrogate compounds like PCBz or PxCP are predominantly formed in parallel during *de novo* synthesis[7-11]. In particular PCDF and PCBz show a close correlation in *de novo* experiments over a wide temperature range (Figure 1)[11]. This is the reason and basis that a correlation of PCBz and TEQ (PCDF normally account in stack gas of MWI for more than 75% of TEQ[2]) exists in incinerators.

However, the ratio of PCBz to PCDD/PCDF was found to differ up 5 fold when comparing fly ashes from different incinerators and types of incinerators in *de novo* synthesis experiments (Figure 2). This indicates that the composition of the fly ash, possibly related to differences in waste feed or process conditions, can have a significant effect on the ratio of PCDD/PCDF and surrogates already in the state of formation.

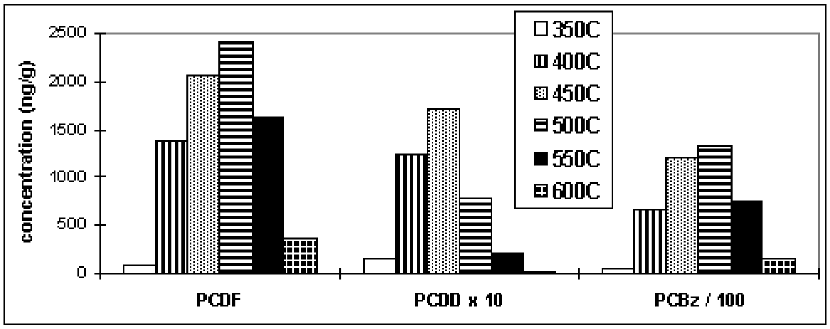

Figure 1: Formation of PCDF, PCDD and PCBz in *de novo* experiment in laboratory[11].

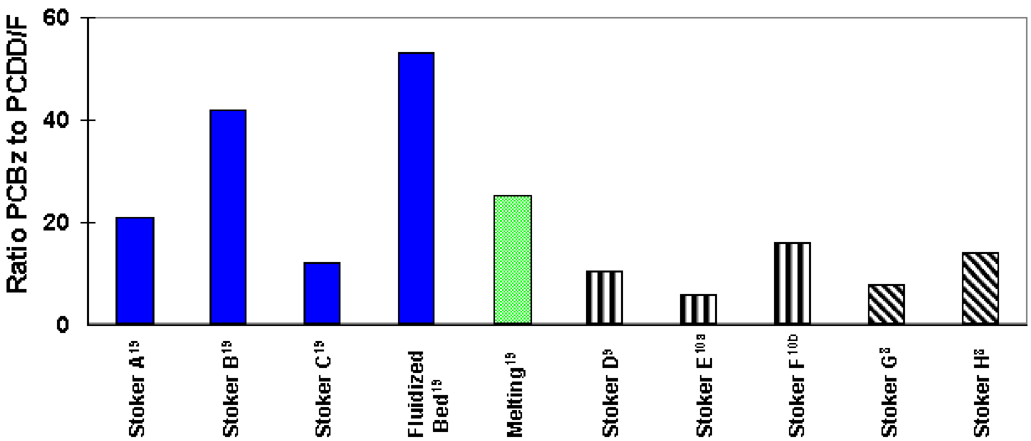

Figure 2: Correlation of PCDD/PCDF (STetra to Octa) and PCBz (SDi to Hexa) in *de novo* experiment of fly ashes from different incinerators and one pyrolysis melting plant[8-10, 19].

2) Impact of memory effects on time frame of PCDD/PCDF and surrogate emission

One key question for the use of on-line measurement for system control (furnace or post combustion control) is the time frame of formation and emission of PCDD/PCDFs (and surrogates). Several research studies have shown that the emission of PCDD/PCDFs lasts for hours after furnace disturbance, even if measurements are conducted in the high temperature zone[12]. Furthermore, it was found that the PCDD/PCDF emission can have a time delay of hours after disturbed combustion condition[13], and that after start-up, the peak concentrations of PCDD/PCDF emission can occur with a 4 to 5 hours delay compared to the maximum CO and the hydrocarbon emission curves[14]. The time delay caused by *de novo* based memory effects[13] in the flue gas line (in boiler, gas cooler, reheater; T > ca. 200°C) is one reason why an operation control of the furnace by on-line measurements of PCDD/PCDF or surrogates is not feasible.

Furthermore, adsorptive memory effects[13] of PCDD/PCDFs have been observed and described e.g. in wet scrubbers[15-18] and can be expected for the entire post combustion section and flue gas line, up to about 400ºC (gas cooler, duct pipes, wet scrubber, bagfilter, reheater). Due to the low volatility of PCDD/PCDFs, these adsorptive memory effects can last for days to weeks for wet scrubbers[17]. It was discovered that these memory effects differ considerably for the different PCDD/PCDF homologues and lead to significant shifts in the homologue pattern of PCDD/PCDF over the time of the memory effects. Therefore, the emission characteristics of memory effects are different for the different homologues of the same compound class and depend on differences in volatility caused by degree of chlorination. This questions the feasibility of using on-line measurement of low chlorinated PCDD/PCDF as surrogates[6] for accurate prediction of TEQ emission. Furthermore, it can be expected that the low volatile mono aromatic surrogates like PCBz and PxCP (In addition to differences in adsorption, the chlorophenols have different chemical behaviour in wet scrubbing systems and have high removal efficiencies in alkaline scrubbing solution) will show significantly different adsorption/desorption behaviour along the flue gas line compared to PCDD/PCDFs (TEQ). The study of Takaoka et al.[16] indicates that PCBz and PCP do not show significant memory effects even in wet scrubbers (the APCD operated at lowest temperature), and it is uncertain whether these surrogates have any relevant adsorption based memory effect at all.

These differences in adsorption/desorption behaviour of PCDD/PCDF and surrogates pose the question of whether a close time related relationship exists between these compounds, and indicate that the ability of surrogates to predict the final emission characteristics of PCDD/PCDF in stack gas remains insufficient. More investigation is necessary to understand time frame of emission characteristics of PCDD/PCDF and surrogates and the impact of these factors on their relationship to provide a clear concept of the limitations and options of surrogate measurements.

3) Removal of PCDD/PCDF and surrogates by air pollution control devices (APCD)

The impact of emission control devices on the ratio of PCDD/PCDF (TEQ) to surrogates was previously discovered by Kaune et al.[1] and Blumenstock et al.[2]. Kaune et al.[1] investigated the effect of activated carbon on the correlation of P_5CBz to PCDDs/PCDFs (TEQ value) and found a considerable impact from the use/not use and even the way of application of activated carbon. Blumenstock et al.[2] reported on the fundamental impact of a wet scrubber on the correlation of chlorophenols to TEQ (especially low chlorinated chlorophenols) and concluded that chlorophenols were not a reliable indicator in stack gas of the investigated incinerator. These impacts are not identical with memory effects, which only lead to a shift in the time frame of emission characteristics. Rather, they impact on the elimination of PCDD/PCDF and surrogates by the APCD, due to differences in the removal/destruction efficiency. Both effects (memory and removal characteristics) are, however, interrelated since both are mainly caused by the different volatility of PCDD/PCDF and surrogate compounds. The APCD are typically optimised for PCDD/PCDF removal/destruction to comply with the respective emission limits. The removal efficiency for the indicator compounds, however, can differ considerably from those for PCDDs/PCDFs. For example, our previous investigations[18] showed the removal efficiency of the bag filter (160°C; activated carbon spray) for PCDDs/PCDFs (and TEQ) in the investigated municipal waste incinerator to be more than 99%, while the removal efficiency for chlorophenols (di to penta) and chlorobenzenes (di to hexa) ranged from 75 to 95%. This results in a 5-25 fold shift of the ratio of PCBz homologues to PCDD/PCDFs. In addition, the destruction efficiency of the SCR catalyst (225°C) for PCDDs/PCDFs was found to be around 90%, while the destruction efficiency for the PCBz ranged from 17 to 30% (Figure 3). This results in a similar shift of the ratio of PCBz homologues to PCDD/Fs. Therefore, the APCD has a significant impact on the ratio of PCDD/PCDF (TEQ) to surrogate emissions, which can lead to a change in the ratio of PCDD/PCDF (TEQ) to surrogates of more than one order of magnitude.

Since APCD and operation conditions differ from one incinerator to another, the correlation of PCDD/PCDF (TEQ) and surrogates would have to be established and validated for each single incinerator, and each change in the air pollution control (engineering or operation) may require a new validation of the correlation.

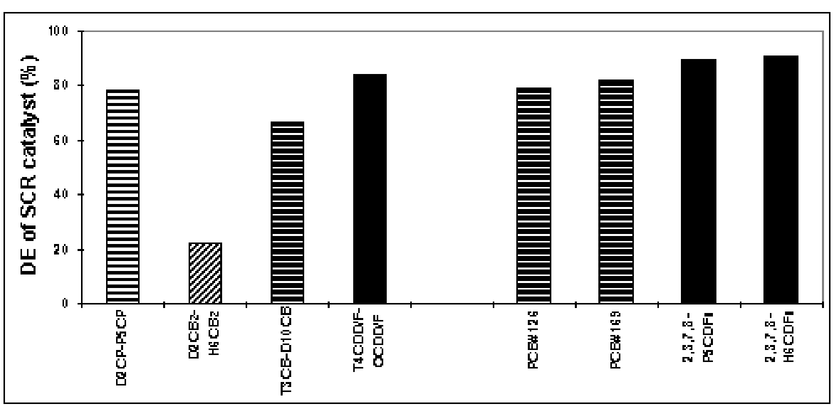

Figure 3: Destruction efficiency of the SCR-catalyst (225°C) for chlorophenols, chlorobenzenes, PCBs and PCDD/PCDF and comparison of removal efficiency for PCB#126, PCB#169 and 2,3,7,8-substituted P_5CDF and

H_6CDF[18].

Conclusions

The observed differences in the ratio of PCDD/Fs to surrogates of about one order of magnitude within the same incinerator can be explained by the impact of memory effects on the emission of these compounds as well as differences in their formation characteristics. When comparing different incinerators, the additional impact of APCDs can explain the differences in the ratio of PCDD/PCDF (TEQ) to surrogates of up to two orders of magnitude.

The impact of memory effects, the differences of formation characteristics and the influence of emission control devices on the relationship of PCDD/PCDF (TEQ) and surrogate emissions have to be thoroughly investigated and understood before surrogates might be used for a reliable indication of PCDD/PCDF emission. This relationship would probably have to be investigated for each incinerator before a meaningful relationship of surrogates and TEQ emission can be established. It is however doubtful if these correlations could be used for compliance measurements, due the above described complexity of the interrelationships. On the other hand, after considering and evaluating all three effects, on-line measurement data of PCDD/PCDF and surrogates may be able to provide a more detailed understanding of an incinerator.

In particular the de novo based memory effect in the high temperature zone is one important reason that an on-line measurement of PCDD/PCDF or surrogates would not directly lead to a process control (control of the combustion zone or post combustion section).

Therefore it remains uncertain if the effort and cost of on-line monitoring systems can be justified considering the potential outcome. In this respect it should be evaluated if data from long term monitoring may provide a similar insight into PCDD/PCDF emission characteristics and operation specifications of incinerators (see e.g.[17]) and other thermal sources (metal industry, cement kilns, power plants etc.), and in parallel guarantee a complete supervision of PCDD/PCDF, PCB and surrogate emissions of a plant, as well as provide the TEQ data for compliance measurements.

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