APPLICATION OF MONOCHLOROBENZENE AS A RELIABLE SURROGATE FOR THE PREDICTION OF THE I-TEQ VALUE IN COMBUSTION FACILITIES

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Introduction

In the last two decades efforts have been made to estimate the toxic emission from waste combustion processes via surrogates in order to reduce the time and cost intensive sampling, clean-up and analyzing processes, e.g. for polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/F)(1),(2),(3). By using a coupling of laser ionization and a time-of-flight mass spectrometer (**R**esonance **E**nhanced **M**ultiphoton **I**oniziation-**T**ime **O**f **F**light **M**ass **S**pectrometry, **REMPI-TOFMS**) it is possible to measure products of incomplete combustion (PICs), such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated benzenes and biphenyls (PCBz) real-time on-line during combustion processes. The REMPI-TOFMS instrument was successfully applied for the monitoring of PAH in flue gases of incineration plants (4,5).

PCBz were known as surrogates for the I-TEQ emission of PCDD/F and are therefore target compounds for the monitoring with the REMPI-TOFMS instrument(2,3). The here presented study combines the results of conventional analytical results for chlorinated aromatics (PCDD/F, PCB, PCBz and PCPh) and of REMPI-TOFMS chlorobenzene monitoring.

A hazardous waste and municipal waste incinerator were investigated in this work. Nevertheless, it should be noted that the measurements illustrated here do not allow conclusions to be drawn about plants of this type under normal operation. The here presented data were results from difficult operating conditions selected for test purposes.

This work tries to achieve two main aims: First to show that monochlorobenzene (MCBz) is a reliable surrogate for the I-TEQ emission and to elucidate, why MCBz is a surrogate. Second to prove the practical application of the REMPI-TOFMS instrument for an indirect real-time monitoring of the I-TEQ.

Methods and Materials

The two plants, named as plant A and plant B in the following text, have a thermal power of 22 and 24 MW respectively. At both plants the sampling points were located at the end of the boiler regions, with temperatures around 560K for plant A and 500K for plant B.

The samples were taken isokinetically for conventional analysis. For detailed description of the sampling, clean-up and analyzing procedure see reference(3). All samples were analyzed for PCDD/F, PCBz polychlorinated biphenyls and phenols (PCB and PCPh) from monochlorinated to fully chlorinated homologues.

For the data of the plant B a principal component analysis (PCA) was carried out for all samples taken (flue gas at 1100K and 560K, stack gas at 350K, in total: 51) with the full number of variables (analyzed isomers, homologues and I-TEQ values) available for one sample (334 variables). PCA condenses the information of the complete data by calculating an n-dimensional (n = number of variables) vector space describing the variance of the data set. Accordingly the first principle component represents the greatest part of the explained variance for the data set, the second principle component the second greatest part and so on. Two plots are obtained from PCA, first the loading plot which shows the realtionship between variables (analyzed compounds) and second the score plot, which describes the relation between the cases (analyzed samples).

The sampling for the REMPI-TOFMS measurement was carried out in parallel to the one for the conventional measurements with a quartz glass tube connected with a heated transfer-line which consists of an fused GC capillary column (500 K). Particulates were separated from the flue gas by filtration with a quartz glass filter.

An effusive gas beam was used as an inlet into the TOFMS system. The target compounds were ionized with a tuneable laser system that consists of an Nd:YAG (355nm) pumped dye laser achieving the resonance wavelength of MCBz (@269.82nm). Selective detection of chlorinated aromatics require a tuneable laser system because they show in the applicated wavelength region very distinct UV absorption bands. The repetition rate of the laser was 10Hz. Detection limits for the MCBz with REMPI-TOFMS system described here are in the 100 pptv range. For further detail of the experimental setup and the spectroscopic properties of the compounds see reference (6,7).

All concentration data are normalised to dry air, 1013 mbar, 273K and 11% O_2. Standardization of the data for PCA analysis was performed by means of centering the respective variable.

Results and discussion

Figure 1 shows the regression lines between MCBz and the I-TEQ value for the two incineration plants.

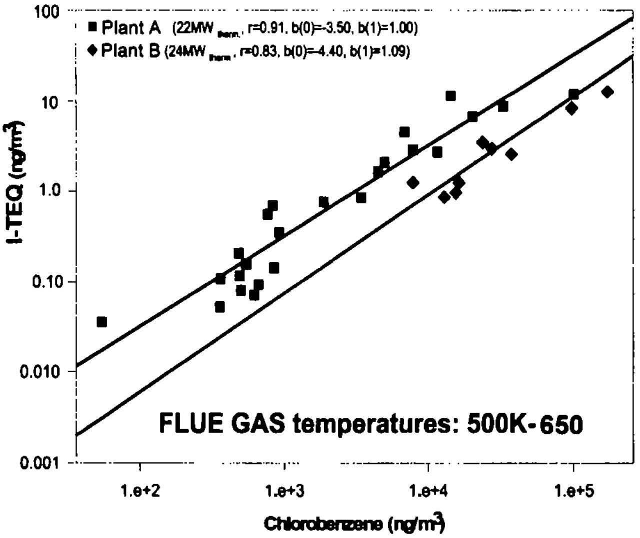

Figure 1: Regression lines and coeffecients of MCBz as surrogate for the I-TEQ value. ***Please note:*** *All concentration illustrated refer to measurements points upstream of the flue gas cleaning system. The corresponding clean gas emissions are significantly lower than the above shown and meet the regulations. The measurements illustrated do not allow conclusions to be drawn about plants of these types under normal conditions.*

High correlation coefficients were found for these two plants with r = 0.83 (plant A) and 0.91 (plant B). It is noteable that MCBz levels and the corresponding specific regression lines for the I-TEQ are different for the two plants. Furthermore the concentration range of MCBz in plant A measured at the end of the boiler was on average higher than in plant B. This result have to be confirmed by further measurements on this and other plants. To summarize the obtained regression results MCBz can be used as a reliable surrogate for the prediction of the I-TEQ in the investigated combustion facilities.

Figure 2 depicts the results of the PCA analysis (loading and score plot) for the plant A as described in *methods and materials.*

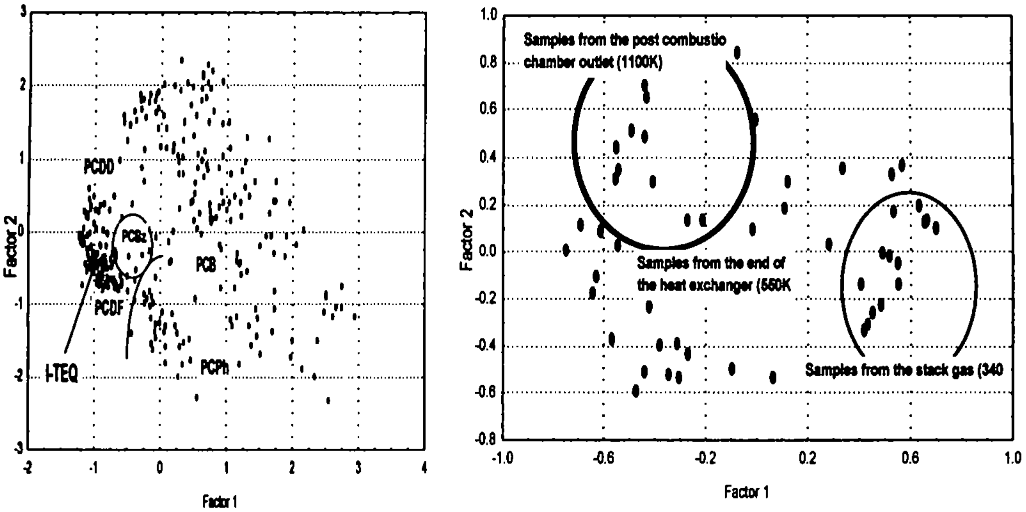

Figure 2: PCA plots (left: loading plot; right: score plot) for PCDD/F, PCB, PCBz and PCPh at plant A (explained variance: PC 1: 24%, PC 2: 13%).

The loading plot depicts that different chlorinated aromatics show a distinct behaviour in the flue gases of plant A. As recently shown the highest variability in all classes of chlorinated aromatics was observed for the PCBz (8). In contrast to that a very uniform behaviour of the variables was detected for the PCDF and PCDD isomers, which is in accordance with the results shown in the literature (9).
The PCBz isomers and homologues were grouped close to the PCDF data points. Furthermore it must be mentioned that the I-TEQ value is carried more than 70% by the toxicitiy of the PCDF. The last two results give hints for a better understanding of the high correlation coefficients between MCBz and the I-TEQ.
In the score plot it is indicated that the location of the sampling points in the plant strongly influences the emission pattern because the points of the cases from the same sampling point are grouped together.
Additionally it was observed that the quantity of PCDF and PCBz was always relatively higher (10 to 1000 times) in the post combustion zone (1100K) than the quantity of PCDD and PCPh, respectively The PCDD and PCPh showed an increase in concentration from 10 to 13 times from the post combustion chamber outlet to the end of the boiler, whereas for PCDF, PCBz and PCB this increase was in the range of 5 to 8 times. The similarities in the formation pathways may be an explanation for the observed close relation of the I-TEQ and the PCBz concentrations (7).

In order to show the practical applicalibility of MCBz as a target surrogate for REMPI TOFMS on-line monitoring, two MCBz real-time on-line measurement sequences in the flue gases were depicted in figure 3 (plant A and B).

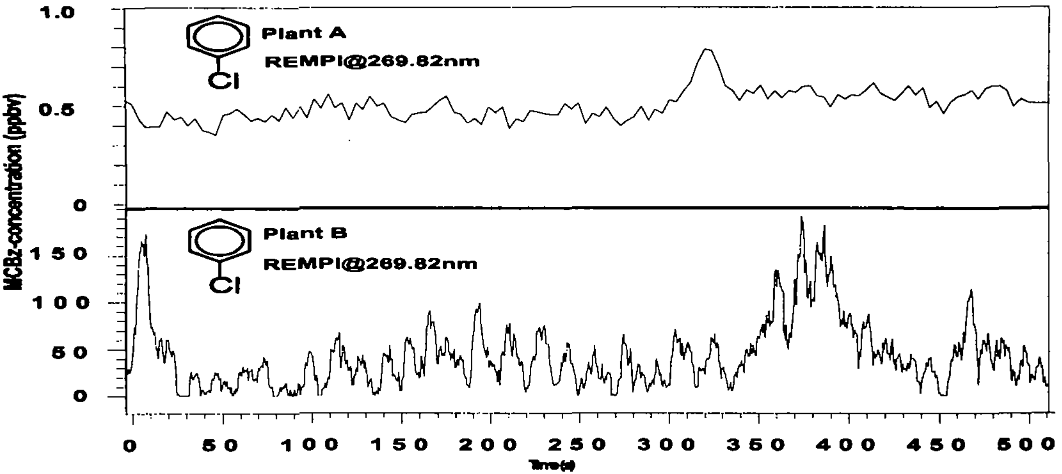

Figure 3: REMPI-TOFMS 112 MCBz mass traces from two different incineration plants during different operation conditions.

In the figure above the MCBz was measured for 500 seconds at different concentration levels at two different plants under very distinct operation conditions. The averaging of the obtained data points from the single laser shots (10Hz) was done in intervals of 5 seconds (plant A) and 1 second (plant B) because of the lower concentration of MCBz in plant A a higher time span was used. In the time scale of seconds fluctuations of the MCBz concentrations are observed for both plants. If MCBz concentration levels of the conventional analysis (figure 2) and REMPI-TOFMS results (figure 3) were compared, they match each other in a wide concentration range very well (range factor of 100). The good accordance in the concentration ranges of both techniques shows future possibilities and the reliability of monitoring surrogates in incineration processes with REMPI-TOFMS.

The main results of the presented study are:

1. Monochlorobenzene is a surrogate for the prediction of the I-TEQ value of different combustion facilities with a high predicition accurancy (r = 0.83 - 0.91). One explanation of the first result might be that the main part of the toxicity from the I-TEQ value is carried by the PCDF (>70%).
2. The REMPI-TOFMS instrument can be used as MCBz monitor for indirect measurement of the I-TEQ value in full scale combustion plants.

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References

(1) Öberg, T.; Bergström, J. *Chemosphere* **1989**, *19*, 337-344.
(2) Kaune, A.; Lenoir, D.; Nikolai, U.; Kettrup, A. *Chemosphere* **1994**, *29*, 2083-2096.
(3) Blumenstock, M.; Zimmermann, R.; Schramm, K.-W.; Kaune, A.; Nikolai, U.; Lenoir, D.; Kettrup, A. *Journal of Analytical and Applied Pyrolysis* **1999**, *49*, 179-190.
(4) Zimmermann, R.; Heger, H. J.; Kettrup, A.; Boesl, U. *Rapid Communications in Mass Spectrometry* **1997**, *11*, 1095-1102.
(5) Heger, H. J.; Zimmermann, R.; Dorfner, R.; Beckmann, M.; Griebel, H.; Kettrup, A.; Boesl, U. *Analytical Chemistry* **1999**, *71*, 46-57.
(6) Zimmermann, R.; Heger, H. J.; Blumenstock, M.; Dorfner, R.; Schramm, K.-W.; Boesl, U.; Kettrup, A. *Rapid Communications in Mass Spectrometry* **1999**, *13*, 307-314.
(7) Blumenstock, M.; Zimmermann, R.; Schramm, K.-W.; Kettrup, A. *Chemosphere* **1999**, in press.
(8) Blumenstock, M.; Zimmermann, R.; Schramm, K.-W.; Kettrup, A. *Organohalogen Compounds* **1999**, *41*, 87-95.
(9) Wehrmeier, A.; Lenoir, D.; Schramm, K.-W.; Zimmermann, R.; Hahn, K.; Henkelmann, B.; Kettrup, A. *Chemosphere* **1998**, *36*, 2775-2801.