

ONLINE MEASUREMENT SYSTEM FOR PCDD/F AND OTHER ORGANIC POLLUTANTS IN STACK GASES OF WASTE INCINERATORS AND THERMAL PROCESSES

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Introduction

Polychlorinated dioxins and furans have been observed to be formed as unwanted products of incomplete combustion in nearly all incineration and thermal processes. Due to their highly toxic and persistent nature, the amount of dioxins and furans emitted by a process is often used as a standard for its ecological valuation. Therefore in several countries an emission limit value for dioxins and furans emitted by a thermal process exists. In Germany for example the emission limit value is 0.1 ng I-TEQ/m_N. This value was adopted by the European Commission for an extensive european legislation. Whereas in the past, stack emissions of PCDD/F have mainly been minimized by costly tailend clean-up technologies, interest now gradually shifts towards emission reduction by optimization of the combustion process. However, definition of inhibiting operation conditions needs improved understanding of the correlation of PCDD/F formation and combustion parameters. The online measurements of PCDD/F profiles necessary to enable a continuous process optimization require fast, flexible and inexpensive analytical methods.

Methods and Materials

At the Institut WAR, Darmstadt University of Technology a continuous measurement system for the determination of polychlorinated dioxins (PCDD) and furans (PCDF) in stack gases of waste incinerators and thermal processes was developed^{1,2}. This emission measuring device consists of three components, the continuous sampling device to generate the stack gas condensate, a HPLC-clean-up device for the enrichment of the PCDD/F and the separation of the residual organic compounds and a mass spectrometer connected by a LC/GC-coupling to determine the amount of PCDD/F by a corresponding indicator isomer. Altogether, the I-TEQ values calculated from the indicator isomer concentration of the emission measurement device are in excellent agreement with those measured by the European guideline DIN EN 1948³.

Two typical isomer profiles of the seventeen I-TEQ-relevant isomers of dioxins and furans are shown in figure 1 (left hand site: municipal waste incineration plant; right hand site: industrial incineration plant for liquid and gaseous chlorinated hydrocarbons) As can be seen, the isomer profiles of the two combustion plants are constant. Generally all plants shows this effect if they are working under constant operation conditions. For this reason the total I-TEQ value can be calculated only from one of these isomers with a sufficient certainty.

As an indicator isomer one has to choose the compound which has the highest contribution to the I-TEQ. For the represented municipal waste incineration plant it is 2,3,4,7,8-pentafuran, for the industrial incineration plant 1,2,3,4,6,7,8-heptafuran.

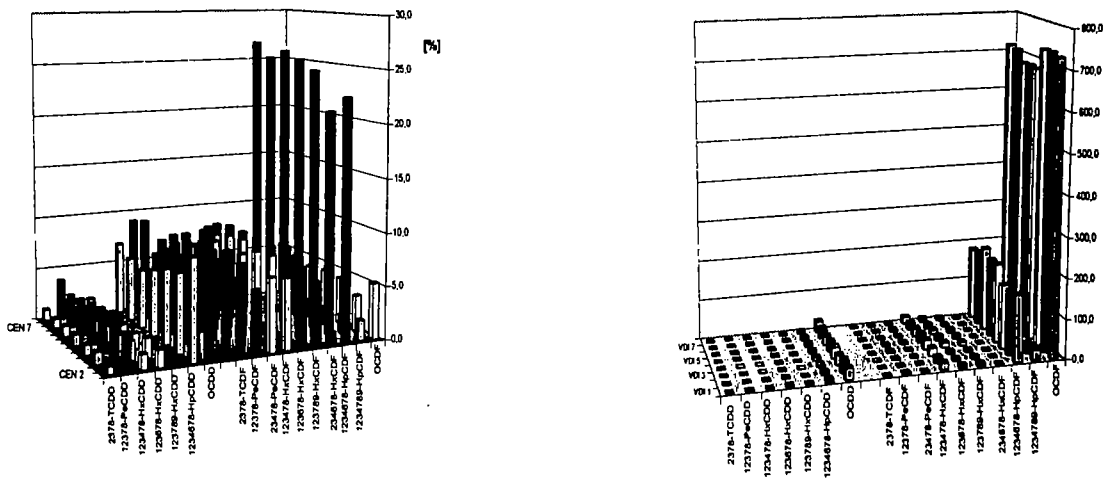


Figure 1 Profile of the seventeen I-TEQ-relevant isomers of dioxins and furans
 left hand site: municipal waste incineration plant
 right hand site: industrial incineration plant for liquid and gaseous chlorinated hydrocarbons

Figure 2 shows the flow sheet of the emission measuring device. It consists of three components described above.

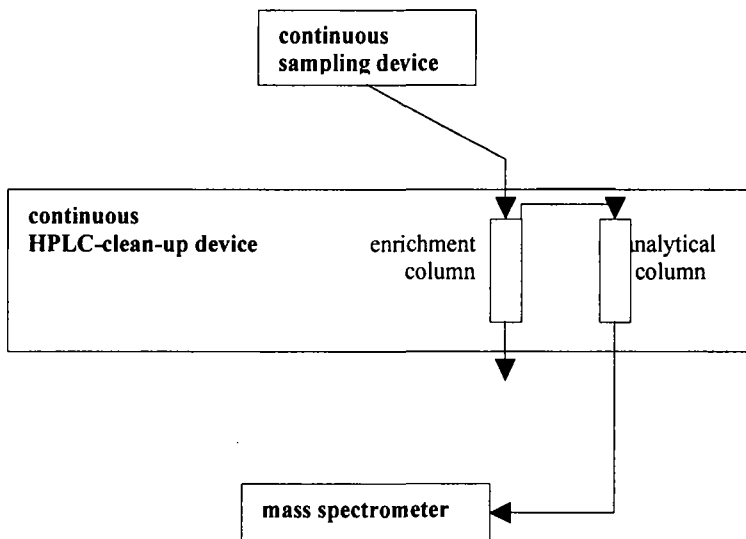


Figure 2 Flow sheet of the emission measuring device

One of the crucial problems was to develop a sampling device which shows no adsorption effects. Already during the development of the clean-up device it was found that the recovery rate of the indicator isomer was only 20 – 25 %. The major part was found to adsorb on the glass surface of

the specimen glass. Adsorption on surfaces of dioxins and furans represents a major problem for the continuous operation of the sampling device. By adding a defined percentage of gaseous methanol to the stack gas adsorption processes can be suppressed during the condensation in the sampling device.

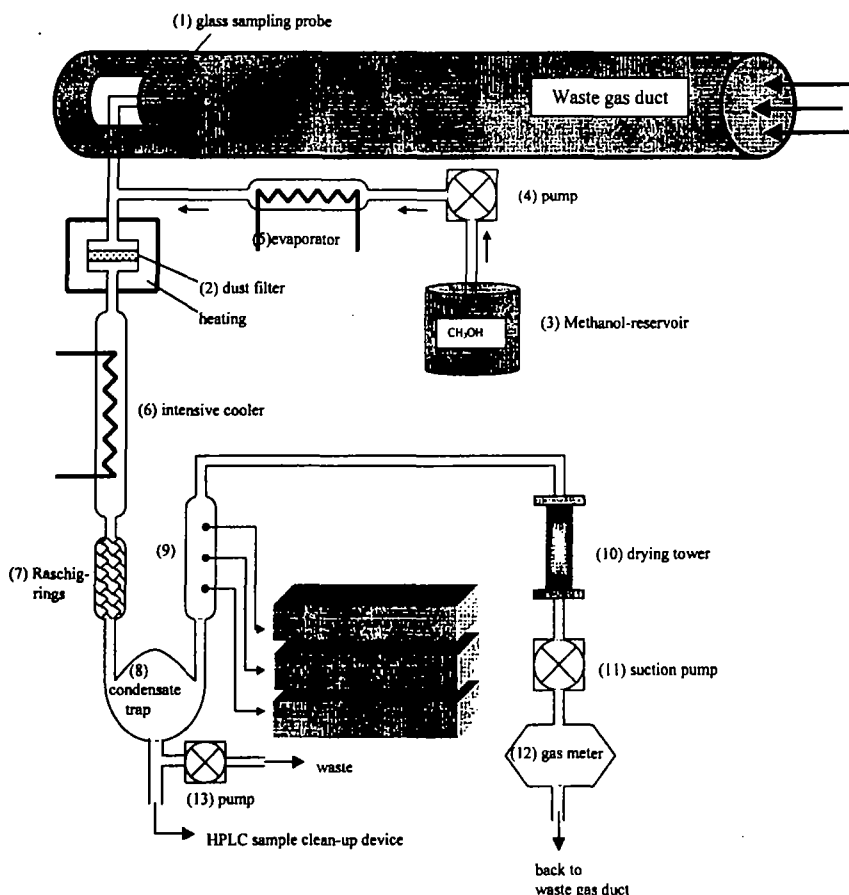


Figure 3 Arrangement of the continuous sampling device

Figure 3 illustrates the developed continuous sampling device based on the facts described above. The continuous sampling device has been installed for a period of two months directly upstream of the suction blower of a municipal waste incineration plant. In this period two sample collection series were performed during routine operation. During the first measuring period no gaseous methanol was added in order to obtain the PCDD/F content of the pure condensate (**condensate method**). Whereas the second measurement program included the methanol addition (44 wt. % for pentafuran) to investigate the influence on the PCDD/F extraction capacity (**methanol method**). Furthermore the continuous sampling device including the HPLC-clean-up device has been installed for one month at the stack of an industrial incinerator for liquid and gaseous chlorinated hydrocarbons to do the first online clean-up (methanol content 57 % for heptafuran).

During both measuring campaigns parallel samplings according to the european guideline DIN EN 1948 were performed simultaneously at the same place.

Results and Discussion

By adding gaseous methanol to the stack gas (methanol method) 95 % of the PCDD/F are found in the condensate instead of 30 % without methanol addition (condensate method). Figure 4 shows the results of the measurements at the industrial incinerator for liquid and gaseous chlorinated hydrocarbons. The sampling device was prepared to generate a condensate with 57 wt.-% methanol which is the optimum for the indicator isomer 1,2,3,4,6,7,8-heptafuran.

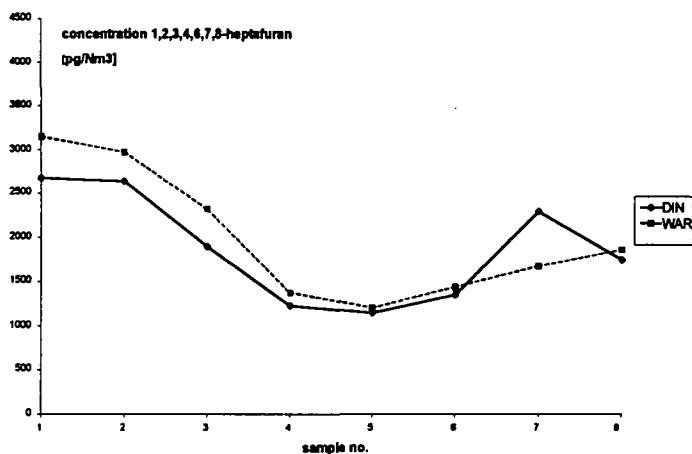


Figure 4 Results for the indicator isomer 1,2,3,4,6,7,8-heptafuran
 - online measurement (methanol method)
 - DIN EN 1948 guideline

As can be seen, the results are in excellent agreement with those measured by the european guideline DIN EN 1948 except of sample 7. During this measurement the sampling device generated a condensate which had a methanol content of only 52 wt.-% instead of 57 wt.-%. This leads to adsorption effects and ultimately to losses of heptafuran in the clean-up fraction.

References

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