ONLINE MEASUREMENT SYSTEM FOR THE DETERMINATION OF PCDD/F I-TEQ VALUES IN STACK GASES OF INCINERATION PLANTS BY USING THE CONGENER FINGERPRINT METHOD - LATEST EXPERIENCES -

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Introduction

In many countries there exist an emission limit value for dioxins and furans emitted by a thermal process. For example, in the European Community the emission limit value for waste incinerators is 0.1 ng I-TEQ/m^3_N. Other industrial societies like the United States of America, Japan etc. have emission limit values within the same range. For the determination of the emission values, different standard methods are available in different countries. All these methods are very expensive and time consuming. Usually, it takes five to seven days after sampling to obtain the result. A continuous measurement system for the determination of PCDD/F in stack gases of waste incinerators and thermal processes developed at the Institute WAR, Darmstadt University of Technology has been recently described [1,2].

Methods and Materials

Modern continuously operating incineration plants, while working under stable operation conditions, always demonstrate the same congener pattern (see figure 1). However, the congener pattern differs extremely from plant to plant (compare figure 2 with figure 1). Moreover, it has been found that similar types of incineration plants produce similar congener group patterns. For example, the characteristic profile of the chlorinated homologues of PCDD/F from a municipal waste incinerator could be described by[3]:

- PCDF > PCDD

- PCDF: $Cl_4 \cong Cl_5 \cong Cl_6 > Cl_7 > Cl_8$
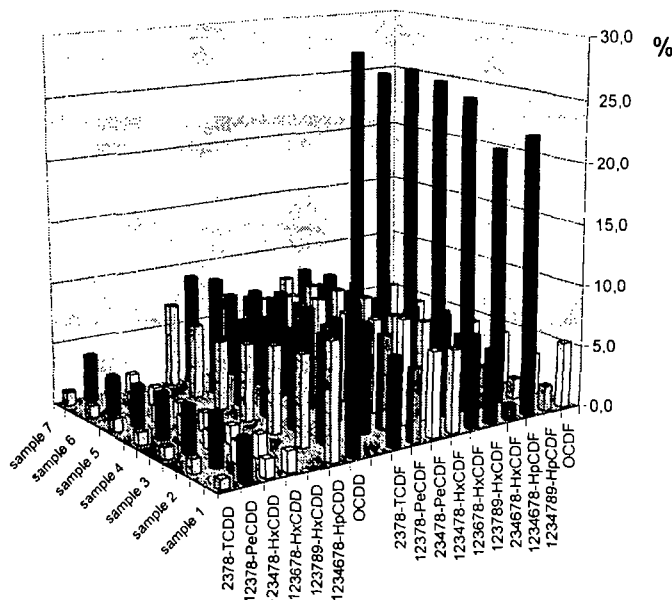
- PCDD: $Cl_4 < Cl_5 > Cl_6 < Cl_7 \cong Cl_8$

Figure 1 *Pattern of the seventeen I-TEQ- relevant*
congeners from seven samplings at the same MSWI expressed
as percentages of the total amount of the measured congeners

In summary, it can be said that every plant has its own congener fingerprint. Once the fingerprint is known, by determining either one of these congeners the total I-TEQ value can be calculated with a sufficient certainty.
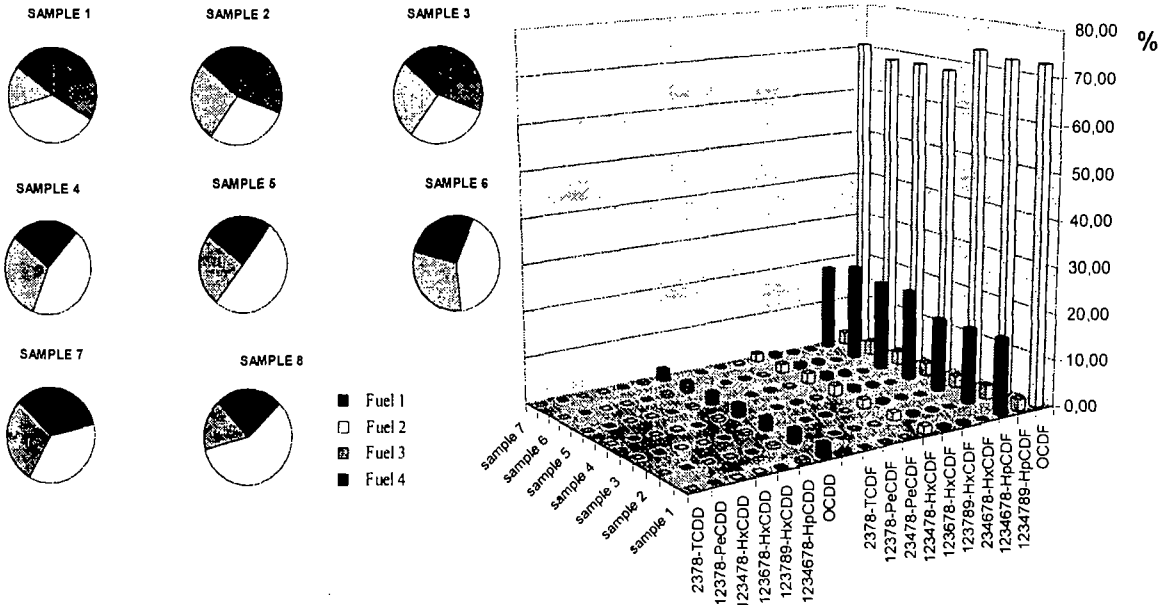

Figure 2 left hand side: right hand side:
Fuel composition during   *Pattern of the seventeen I-TEQ- relevant*
sampling 1-8   *congeners from seven samplings at the same*
• *Fuel 1-4: different*   *industrial plant expressed as percentages of the total*
    chlorinated hydrocarbons   *amount of the measured congeners*

Furthermore, as figure 2 shows, there is no significant influence of the fuel composition on the congener pattern. The reason is that the represented incineration plant is designed to burn special waste mixtures (gaseous and liquid chlorinated hydrocarbons) in a defined range. Of course, the dioxin patterns differ from fuel to fuel and from plant to plant (MSWI, sewage sludge incineration, hazardous waste incineration, etc.) but within the allowed range of the waste mixture of one plant the influence of the fuel composition on the dioxin pattern could be neglected. For example, during a combustion experiment at MSWI Darmstadt, Germany, the share of plastic materials in the fuel was increased from 10 % to 30 % by adding polyvinyl chloride material[4]. Addition of more than 30 % was not feasible due to the load characteristic of the furnace grate. This drastic increase of chlorinated material leads to higher I-TEQ values but it had no effect on the dioxin pattern. Strictly speaking, beside the fuel characteristics there are a number of chemical and physical effects inside an incineration plant which influence the dioxins pattern, such as:

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adsorption/desorption effects on surfaces, catalytic reactions on surfaces and flue dusts, residence time during temperature range of dioxin formation, solubility in the flue gas scrubber, humidity, oxygen content etc. which have an influence on the dioxin pattern. Therefore, it can be said that the components of an incineration plant, especially of the different flue gas purification systems, compensate small variations of the dioxin patterns resulting from the variations in the fuel. For example, investigations at a wet scrubber system showed that the pattern of the PCDD/F differs between the inlet and the outlet of the scrubber system caused by the different adsortion/desorption behaviour of higher and lower clorinated isomers[5].

It is safe to assume that a plant operating under constant conditions always shows the same dioxin pattern and the I-TEQ value can be calculated from only one isomer.
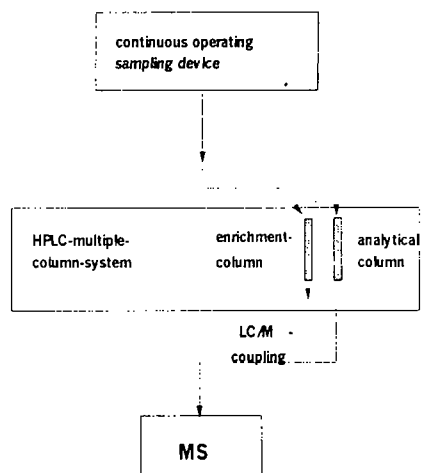

Figure 3: *Flow sheet of the emission measuring system*

Figure 3 shows the flow sheet of the emission measuring system. It consists of three components, the continuous gas 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 the indicator isomer.

Continuous gas sampling device
One of the crucial problems was to develop a sampling device that shows no adsorption effects and generated an optimal sample matrix for the following clean-up device. Contamination effects of PCDD/F at the inner surface of the sampling device caused by the adsorption/desorption equilibrium restoration were found to be the major problem for the continuous operation of the device and were leading to incorrect emission values after very high or low emission peaks. By adding a defined amount of gaseous methanol to the stack gas in the sampling probe contaminations could be eliminated and the extraction capacity of the indicator isomer drastically increased.

Furthermore, by the addition of gaseous methanol to the gas sample, the operation temperature of the intensive cooler could be reduced from –20 °C to –25 °C. In these range of temperatures, nearly all dioxins and furans (96 – 98 %) condense into the liquid phase and thus a downstream adsorption unit (XAD-2, polyurethane foam) is not longer necessary.

Continuous clean-up device
The clean-up of the waste gas condensate/methanol mixture generated by the gas sampling device and the separation of the indicator isomer was carried out by a standard HPLC-enrichment system with an RP-8 (Reversed Phase) enrichment column and a RP-18-ec (Reversed Phase "end capped") analytical column. In contrast to our latest publications[1,2] it turned out that it is better to *choose one of the higher chlorinated congeners* (for example 1,2,3,4,6,7,8 HpCDF) as an indicator instead of the congener which has the highest contribution to the I-TEQ value. The higher chlorinated PCDD/F have longer retention times in the HPLC-System and therefore can be more efficiently separated from the residual organics. Furthermore, the first tests of the long-term

behaviour of the HPLC columns show an amazing stability and repeatability against the waste gas condensate.

Quantification of the indicator isomer

For the quantification of the indicator isomer a LC/GC-coupling system was selected. It consists of a Large-Volume-Sampler (LVS) to transfer the indicator isomer obtained by a "heart-cut" into a Cooled-Injection-System (CIS). The advantage of this coupling system is that no losses of the indicator isomer occur during its transfer into the GC/MS. The indicator isomer was quantified by using an internal ^{13}C-standard which was added with the gaseous methanol during sampling.

Results

The new PCDD/F online measurement system (including the methanol sampling method) calculates the total I-TEQ value from the amount of the indicator isomer. Table 1 compares the I-TEQ values determined by the German standard method (VDI 3499 guideline) and calculated from the concentration of the indicator isomer obtained by the new measuring system. As Table 1 shows, an excellent correspondence between the I-TEQ values determined by VDI and calculated from the new measuring method was achieved. The reasons for this are to be found in the constant congener distribution and the high and constant extraction capacity of the indicator isomer (96%, absolute standard deviation 4.7%).

Table 1 *Comparison of the I-TEQ values determined by VDI and calculated from the new measuring system (seven samplings at the same MSWI)*

sample	I-TEQ determined by VDI [pg/m³]	I-TEQ calculated from new measuring system [pg/m³]
1	129.0	132.5 ± 13.8
2	102.1	103.0 ± 10.8
3	87.9	84.4 ± 8.8
4	81.9	81.6 ± 8.5
5	89.6	90.8 ± 9.5
6	66.6	65.0 ± 6.8
7	73.2	73.9 ± 7.7
8	76.7	76.8 ± 8.0

References

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