

# PROTOTYPE OF A MONITORING SYSTEM FOR ENVIRONMENTAL ORGANIC POLLUTANTS AND POPs IN STACK GASES OF THERMAL PROCESSES

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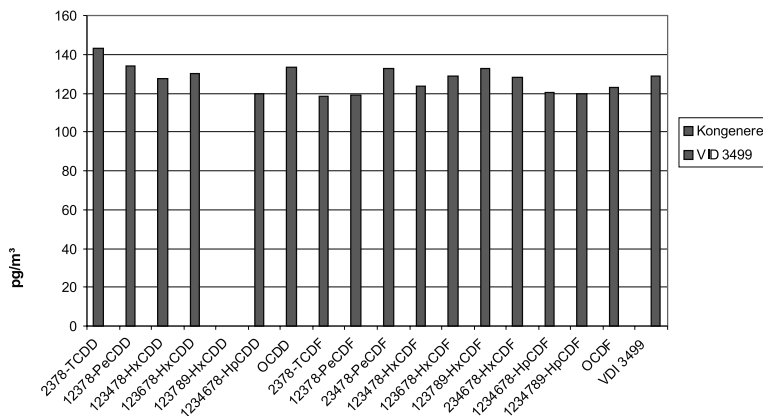
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## Introduction

The Institute WAR, Technische Universität Darmstadt, Germany, had developed a continuous measurement system for the determination of polychlorinated dioxins (PCDD) and furans (PCDF) in stack gases of waste incinerators and thermal processes. The results of this research works had been described in detail in the last three years<sup>1,2,3</sup>. At the time the prototyp of the fully automatically operating monitoring system (*DioxinCop*) is under construction and will undergo a long-term-test in autumn 2002.

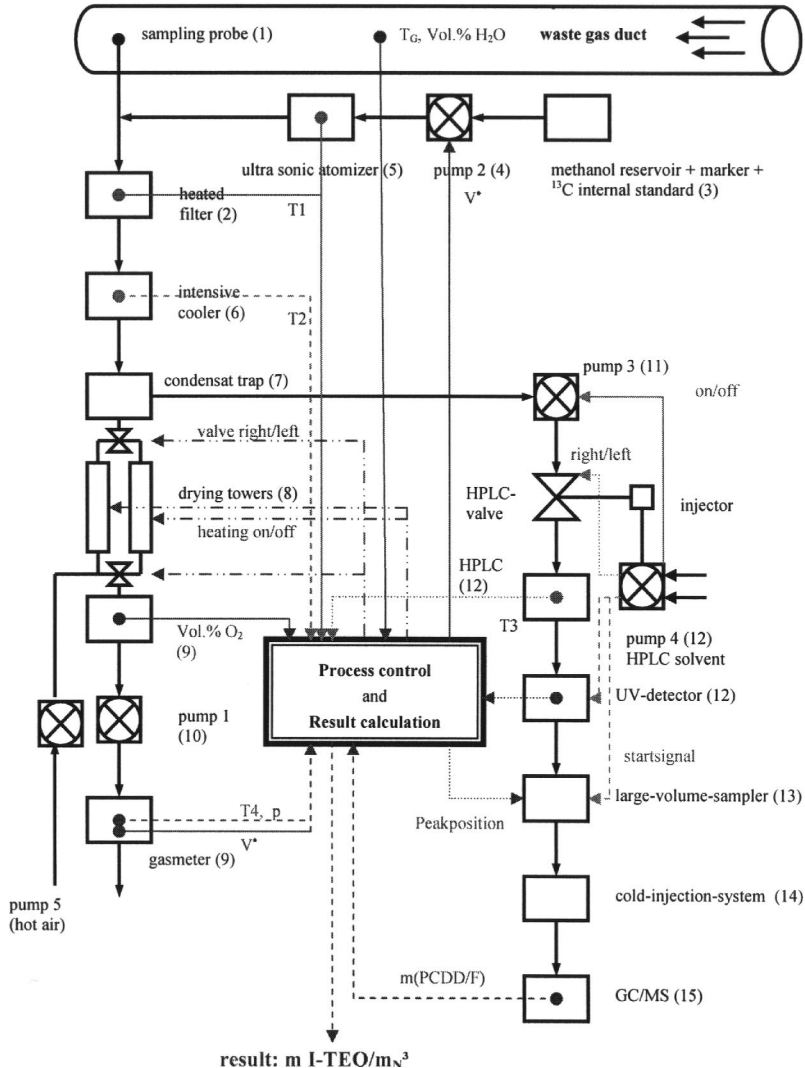
## Methods and Materials

The monitoring system *DioxinCop* consists of three components, a continuous operating 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. Due to the fact that incineration plants which operate under stable conditions show only a very low variation in the presented congener profiles the I-TEQ values can be calculated from only one single congener. Figure 1 shows calculated I-TEQ values from measured single congener amounts in comparison to the determined I-TEQ value by the german standard method VDI 3499.



**Figure 1.** Calculated I-TEQ values in comparison to the standard I-TEQ (VDI 3499)

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**Figure 2.** Flow sheet of the monitoring system *DioxinCop*

Figure 2 illustrates the general flow sheet of the monitoring system *DioxinCop*. The essential part of the monitoring system is the continuous operating sampling device (No. 1-10)<sup>1,2</sup>. Stack gas is continuously and isokinetically extracted through a glass sampling probe (1) with pump 1 (10). A dust filter (2) is electrically heated up to 115 - 125 °C in order to prevent adsorption of PCDD/PCDF on the particles retained. Upstream of the filter a defined volume flow of gaseous methanol is added with pump 2 (4). The methanol (3) including a <sup>13</sup>C-standard PCDD/F isomer and an UV-marker is evaporated in a ultrasonic atomizer (5). This gas mixture is then condensed in an intensive cooler (6) and leads to a condensate containing a defined methanol percentage collected in a condensate trap (7).

The residual sample gas is dried in a system of two drying towers (8). Oxygen content, temperature and pressure (9) were determined to calculate standard conditions. At the bottom of the condensate trap (7), the required amount of condensate can be drained off to the analyzing device (12) (HPLC-system). In order to constantly purge the condensate trap with condensate during continuous operation more sample gas than needed is extracted. Excess condensate can be transferred back into the waste duct.

The HPLC clean-up system (11,12) consists of an enrichment column, a reversed-phase (RP) analytical column and a three solvent gradient pump connected by six-port valve in order to elute the enriched organic compounds to the analytical column. A UV-detector is used to check the state of the analytical column by observing the retention time of the added UV-marker (3). The native PCDD/F indicator isomer and the added  $^{13}\text{C}$ -standard isomer (3) were separated from the other PCDD/F with a so-called „heart-cut“ by the large-volume-sampler (13). The heart-cutted PCDD/F fraction is then transferred to the cold-injection-system (14) of the GC/MS (15). Due to the pre-separation of the HPLC system only a short GC column (DB5) is used to shorten the analysis time.

All functions of *DioxinCop* are computer-controlled. Table 1 shows the main data sets constantly recorded by the monitoring system.

**Table 1.** Main recorded data sets

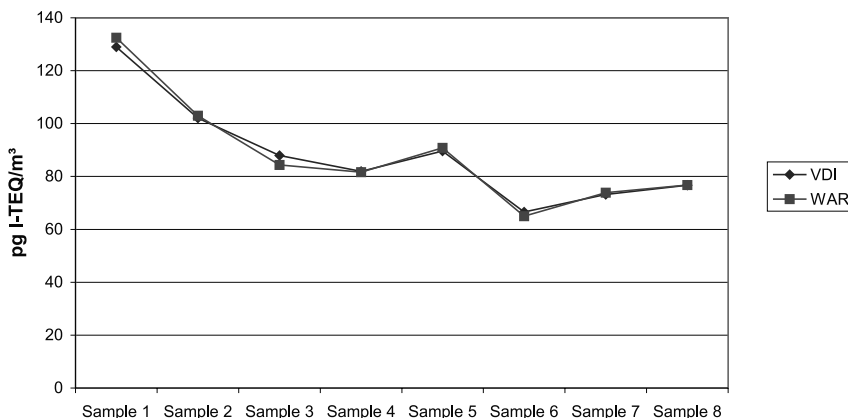
Data set	Used for
temperature sample gas – inlet – ( $T_G$ ) moisture sample gas – inlet – (Vol.% $\text{H}_2\text{O}$ )	to calculate the methanol addition
temperature filter (T1)	to prevent PCDD/F adsorption on particles
temperature intensive cooler (T2)	to control condensing process
temperature sample gas – outlet – (T4)	to calculate the standard volume and standard oxygen condition
standard pressure – outlet – (p) oxygen content – outlet – (Vol.% $\text{O}_2$ ) volume flow sample gas (V)	
start/stop time HPLC enrichment step	to calculate condensed sample gas volume
HPLC chromatogram	to control profile of organic compounds in the waste gas
GC chromatogram	to quantify indicator congener of PCDD/F by comparing the native PCDD/F with the internal $^{13}\text{C}$ -standard

## Results

The measurement system *DioxinCop* calculates the total I-TEQ value from the amount of only one indicator isomer. The results so far showed an excellent agreement with the I-TEQ values determined with the German (VDI 3499) or European (EN 1948) standard method. *DioxinCop* is not a real-time

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measurement system. It generates every 30-45 minutes (depends on enrichment time and retention time of the chosen indicator isomer) one I-TEQ value and is therefore a so-called quasi-continuous monitoring system.



**Figure 3.** compares the I-TEQ values determined by the German standard method (VDI 3499) and measured and calculated from *DioxinCop* (WAR). The monitoring system is registered at the German Patent Office<sup>4</sup>.

## References

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5. German Patent Office, *Registered Design* No. 297 02 315.2, „Device for the quasi continuous measuring of organic and anorganic substances in process gases, especially for polychlorinated Dibenzo-p-dioxins and Dibenzofurans in waste gases of incinerations plants“, 28.05.1997.