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FIRST LONG-TERM FIELD TEST OF THE PCDD/F-ANALYZER DIOXINCOP

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Introduction

The Institute WAR, Technische Universität Darmstadt, Germany, had developed and constructed a prototyp of a continuous measurement system (*DioxinCop)* 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 four years[1,2,3,4]. A long-term field test of this prototyp took place at an industrial hazardous waste incinerator between Septemer 2002 and January 2003.

Methods and Materials

The functionality of the monitoring system *DioxinCop* had been described in detail in the last year[4]. It will be repeated here in short-terms to prevent a lack of understanding. Figure 1 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)[1,2]. 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 ^{13}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 dryed 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). 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}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 transfered 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. *DioxinCop* generates every 70 min one I-TEQ value.

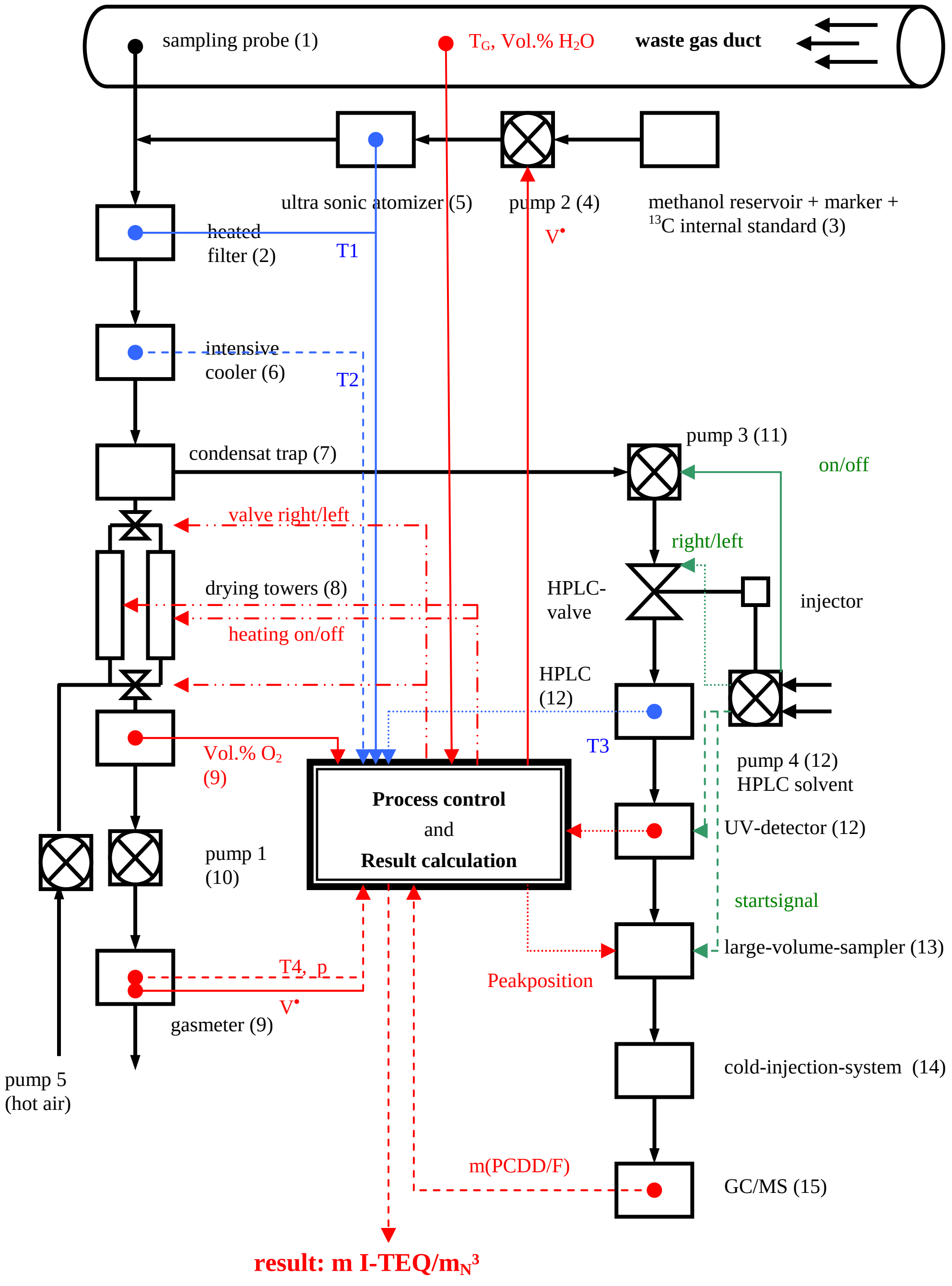

Figure 1 Flow sheet of the monitoring system *DioxinCop*

Results

Figure 2 shows a complete HPLC-chromatogram of one gas sample of the hazardous waste incinerator. The shown peaks represent the enriched condensate from 0,16 m³ waste gas. The retention time frame of the PCDD/F is illustrated in the gray window. Figure 3 shows the marker and the PCDD/F-peaks in an enlarged cutout (gray window) from firgure 1. The peaks of the UV-marker and the HXCDF and HpCDF homologues are marked. As an indicator congener 1,2,3,4,6,7,8-HpCDF was chosen due to its high quantity and high ratio to the total I-TEQ. Cause of the ageing of the HPLC seperation column and the varying initial load of the other organic pollutants inside a sample (see fig. 1), which elutes in front of the PCDD/F fraction, the retention time of the PCDD/F in not stable. By using an UV-marker, which is shown in figure 3, the accurate “heart-cut” position for the PCDD/F is fixed. The *DioxinCop* software detects the UV-marker automatically and calculates from its shift the new “heart-cut” position.

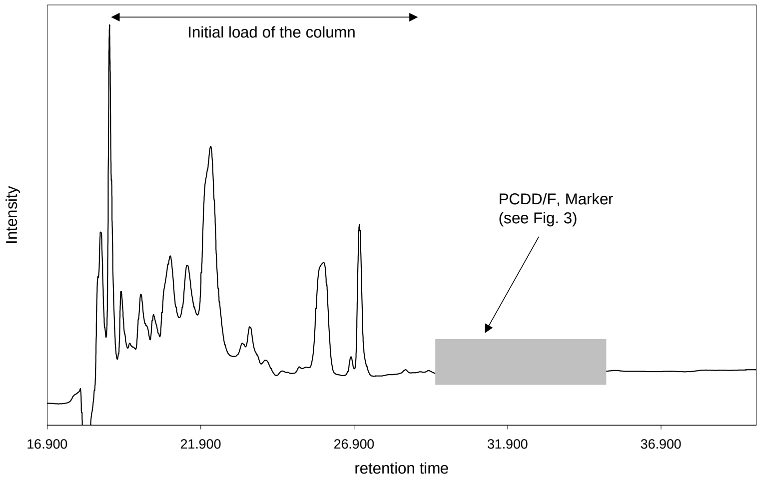

Figure 2
Complete HPLC-chromatogram of one gas sample

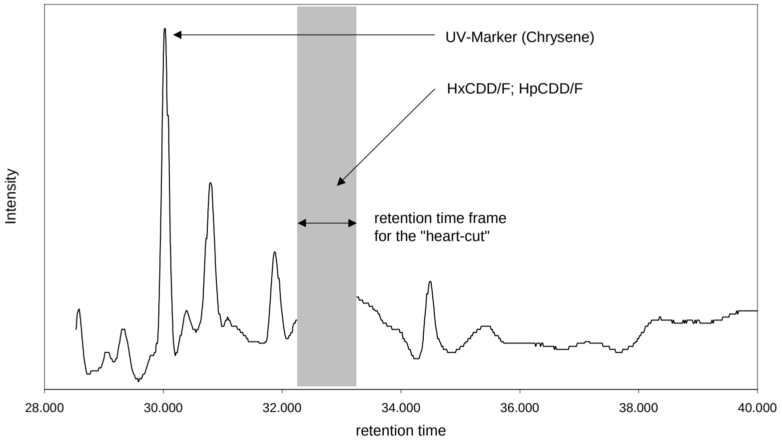

Figure 3
Enlarged cutout of figure 2 (gray window)

A seven days cutout of a three month measuring campaign at an industrial hazardous waste incinerator is shown in figure 4. As can be seen from figure 4, the monitoring system did not see the first zero point measuring . The basic cause of this effect is to find in a contamination of the gas sampling pipe which operates two month without cleaning and leads to the shown memory effect.

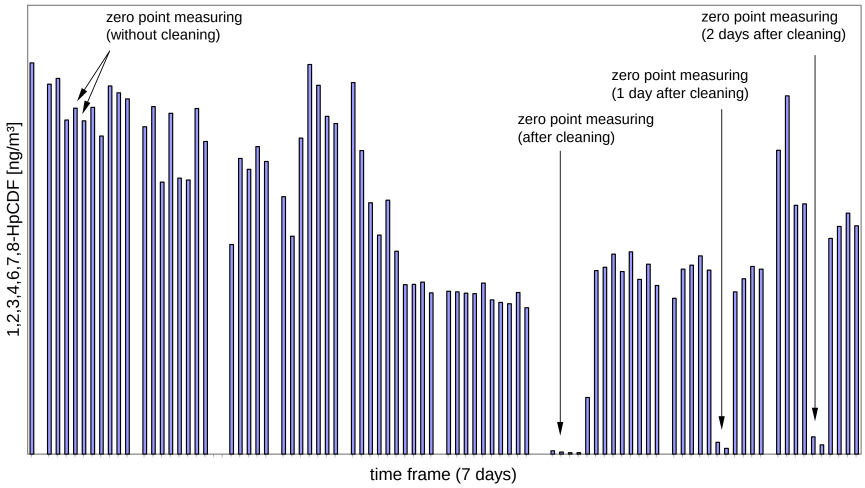

Figure 4 Measuring campaign at an industrial hazardous waste incinerator

By cleaning the gas pipe with acetone the contamination effect could be supressed. An automatic cleaning system was installed in the monitoring system *DioxinCop*. Over the total measuring campaign a great number of operation conditions of the waste incinerator were analyzed. The PCDD/F emissions showed a good correlation with special operation conditions of the plant. Nearly 400 single measurements were realized during the test phase of *DioxinCop*.

References

[1] T. Ludwig, K. Mohr, C. Brockmann, H. Grund, H. Ortner, H. Hoffmann, J. Jager, „Modified Continuous Sampling and Clean-up Device for the Determination of PCDD/F in Waste gases of Incinerators and Thermal Processes“, *Chemosphere* **1999**, Vol. 39, No. 11, 1937-1950.

[2] T. Ludwig, J. Jager, „Online Measurement System for PCDD/F and other organic Pollutants in Stack Gases of Waste Incinerators and Thermal Processes“, *Organohalogen Compounds* **2000**, Vol. 45, 122-125.

[3] T. Ludwig, J. Jager, “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 –“, *Organohalogen Compounds* **2001**, Vol. 54, 355-359.

[4] T. Ludwig, J. Jager, “Prototyp of a Monitoring System for Environmental organic Pollutants and POPs in Stack Gases of Thermal Processes”, *Organohalogen Compounds* **2002**, Vol. 59, 73-76.