

REPRESENTATIVE SAMPLING OF PCDD/PCDF TOGETHER WITH CHLORIDE SALTS IN EMISSION SAMPLES OF MUNICIPAL WASTE INCINERATORS



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INTRODUCTION

The emission of Polychlorinated PCDD/PCDF and PCBs shall be limited as much as possible, to avoid the increase of these components in the nutrition chain. In addition NH_4Cl emissions from stacks shall be limited to reduce the resulting PM_{10} emissions, which are formed during cooling of the stack emissions.

To measure PCDD/F in the emission samples the two following standards are applied: EN 1948 1 and EPA method 23. In the new revision 1 of the EN 1948: Since 2005 this standard has also been able to be applied for long term sampling. To measure NH_4Cl , EN 1911-1 can be used for short term measurement. Up to now there is no long term sampling method available.

As a new sampling technology we present the addition of lime to the mixing chamber, which allows the precipitation of HCl and NH_4Cl together with PCDD/PCDF - including the calculation of the emitted NH_4Cl particles.

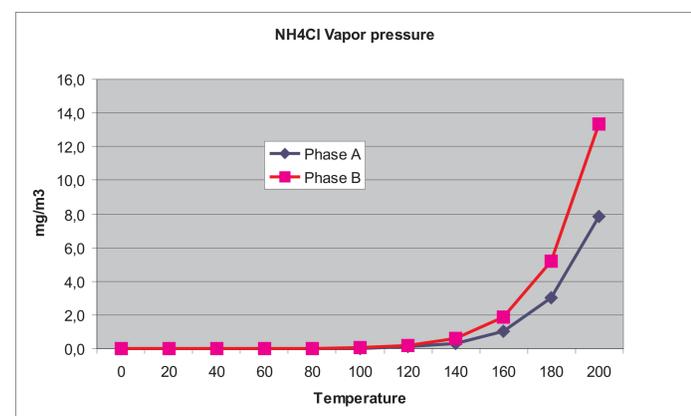
From the homogenised material an aliquot, representing approx. 0,1 g of dry matter is dissolved in 10 ml of pure water and filtered. The solutions are analysed for chloride by Ion chromatographie according EN ISO 10304-2. A sub portion of the homogenized material, representing approx. 0,1 g of dry matter is digested microwave assisted, using high pressure digestion with HNO_3/HCl . The solved metals are analysed by ICP-OES for simultan analysis of them, the rest of the sample is analysed according reference³.



Picture 5: Removal of reacted lime after sampling

RESULTS AND DISCUSSION

Cooling of the flue gas by dilution air to a temperature of 40°C causes the phase transformation of volatile salts to solid dust particles.



Picture 6: Phase equilibrium of NH_4Cl during the cooling to 40°C in the mixing chamber

In modern flue gas cleaning systems, catalysts are used to reduce dioxins and NO_x concentrations of the flue gas. Due to the addition of NH_3 in the catalyst box, remaining HCl is reacting to NH_4Cl , which is volatile at temperatures of 200°C . The DioxinMonitoringSystem cools down the flue gas to 40°C , precipitating the solid particles on a dry filter. This enables the complete sampling of NH_4Cl together with the PCDD/PCDF.

The addition of lime enables the precipitation of HCl , by reaction to CaCl_2 + crystalline water. With this method the total emission of Cl can be measured in combination with the PCDD/F.



Picture 7: Without lime addition



Picture 8: With lime addition

CONCLUSIONS

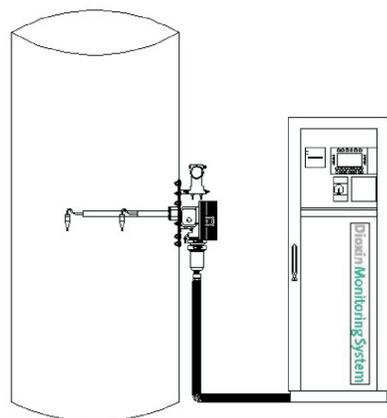
Some measurements in municipal waste incinerators have shown, that particles are passing the dust filter, afterwards they are precipitated on the first polyurethan foam (as picture 7 shows). After adding 10 g of lime, all the particles are precipitated in the mixing chamber before passing the dust filter (as picture 8 shows). In these cases, volatile Al_2Cl_6 and Fe_2Cl_6 was found in the flue gas, which cause a brown precipitate in the filter.

The evaluations of the salt amount have shown, that significant salt emissions are determined, which are not measured by the installed optical dust measurement systems.

Analytical determinations of the composition have shown, that the volatile salt emissions are mainly Cl -salts. Comparing the results with obtained results of the continuous HCl measurement, the portion of Cl -salts can be determined. Their impact to PM_{10} concentrations can be calculated.

REFERENCES

- 1 CEN/TC 264, European standard EN 1948 (2005).
- 2 Kahr, G., Steiner, T. (2001): Obtaining Representative Dioxin Emission Values by the Application of a Modified Installed Sampling System, VDI report 1585.
- 3 Tirlir, W., Donega, M., Voto, G., Kahr, G.: Quick evaluation of long term monitoring samples and the uncertainty of the results, proceedings dioxin (2003).



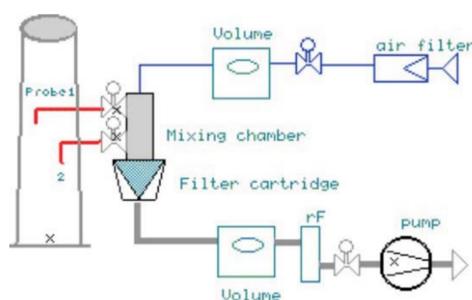
METHODS AND MATERIALS

The DioxinMonitoringSystem[®] is permanently installed on the stack. 2 probes enable a representative sampling of the flue gas at two positions in the stack. The system uses the dilution method of the EN 1948 standard².

Picture 1: DioxinMonitoringSystem[®]

The flue gas is sucked to a mixing chamber, where it is mixed with cleaned dry air to a temperature of 40°C . Afterwards the mixed flue gas/air is filtered by a dust filter and Polyurethan foam.

Dust filter and Polyurethan foam are inserted in a filter cartridge, with a weight of 1700 g. In this application 10 g of "active lime" are added to the mixing chamber, which gives 1710g weight.



Picture 2: Dilution method schematics

After transportation to the plant, the cartridge is inserted to the DioxinMonitoringSystem[®]. The measurement is started.

During the measurement, HCl and NH_4Cl are reacting with the lime to form CaCl_2 + crystalline water. PCDD/PCDF is adsorbed on the freshly formed surfaces. Additionally also other chlorides, e.g. Fe_2Cl_6 and Al_2Cl_6 are reacting with the lime, forming CaCl_2 and corresponding metal oxides.

After 4 weeks sampling, the DioxinMonitoringSystem has sampled approx. 400 m^3 of flue gas. PCDD/PCDF are precipitated completely. Also HCl and NH_4Cl are precipitated completely.

Picture 3: Addition of lime in the cartridge



The measurement is stopped and the cartridge is transported to the laboratory, where the cartridge - together with the filter/foams and the salts - is weighted. After weighting, 1 g of the salt is used for the determination of the Cl , Al and Fe .

The combined material, consisting of crystalline deposits, lime and quartz-wool are transferred to an agate mortar, cut into small pieces by using ceramic scissors, humified by adding 4 g distilled water and afterwards grinded with an agate pestle.

Picture 4: Transportation of cartridge to lab

