Monitoring of different organic compounts

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1. Abstract

In this paper we present an automatic monitoring system that enables both the sampling of PCDD/F according to Draft prEN 1948-1, dilution method and a permanent monitoring over the whole year. To illustrate the possibilities of this method precipitation tests of PAH- and PCB-compounts were performed.

2. Keywords

PCDD; PCDF; sampling; monitoring; DMS; Dioxin Monitoring System

3. Introduction

In recent years, numerous sampling methods have been developed to sample PCDD and PCDF. One of these methods was the dilution method of Lützke[1)]. Based on the dilution method five years ago AE developed an automatic sample taking system. Three years ago AE introduced this sampling techniq as a permanent surveillance system, called DMS[2)]. In the last three years this method was developed to a fully automatic system.

Because of isocinetic sampling and the used dilution method, DMS is able to sample also other organic compunds, like CTPV (coal tar pitch volatiles), PCB`s (polychlorinated biphenyls), organic odour compounts. The use of the dilution method is described in many standards, e.g.:

VDI 3499 part 3, measurement of polychlorinated dioxines and furans
VDI 3873 part 1, measurement of polyaromatic hydrocarbons
CEN 1948-1, determination of the mass concentration of PCDDs/PCDFs

The aim of this work is to show the application of this method to the sampling of other organic compounts.

4. Description of DMS

Now this monitoring system has two principal parts (sample taking unit and conditioning system). The sample taking unit consists of tube, nozzle, mixing chamber, dust precipitator and adsorbtion filters. The flue gas is sucked by isocinetic conditions to the mixing chamber, where it is mixed with clean dilution air. The conditioning system includes the conditioning of dilution air, the pumps for sucking, accurate volume measurement equipment, vents, the control system and documentation. The control system contains the „intelligence", a system which controls the optimum sampling conditions as well as recording all relevant datas.

Table 1: Main functions of DMS
1) the flue gas is cooled to a temperature below 50°C without condensation (inhibitation of reactions between other fluegas compounds and PCDD/F)
2) quantitative accumulation of all PCDD/F by complete dust-precipitation and ad/absorption of gasous dioxins and furans
3) isokinetic sampling to get the right dust quantity
4) stop (stand by mode) in the case of plant shut down oxygencontent > 16 %
5) restart sampling after plant restart oxygencontent < 16 %

5. Procedere for operating DMS

Before sampling the glass fibre filter is spiked with recovery standard (1,2,3,4 ^{13}C-T_4CDD) in the laboratory. The filter is completely prepared by the laboratory and is dispatched to the plant as an easy transferrable unit.

During each measurement-cycle a representative flux is sucked isocinetically out of the chimney. The filter-unit accumulates all of the polychlorinated dioxins and furans (4-8) over the whole sampling period.

At the end of the measurement-cycle (e.g. 14 days) the filter-unit will be exchanged and will be sent to laboratory. To get the correct toxic equivalent the laboratory-results are related to the total volume of the gas sucked and the oxygen content of the flue-gas. To guarantee good measurement quality, the operation in the plant is quite simple:

Table 2: operation at the plant
1) stop the measurement by pressing the OFF- key
2) quality control of the measurement by control of the measurement-protocol
3) remove the loaded filter-unit
4) install the prepared new filter-unit
5) reset all measurement data from the previous measurement-cycle
6) start the new measurement

The permanent monitoring system is fully automatic and works until the next filter exchange during the entire on-stream operation. If a stand by condition occurs, DMS stops the measurement (stand by). If the stand by condition ends, DMS begins the measurement again. If an error occurs, DMS stops the measurement, documents the reason and gives an error message to the operator.

6. Experimental

Due to different kinds of stabilities different methode validations for new other organic compounts were performed. At the first step precipitation tests for different kinds of PAHs and PCBs were performed.

The mean difference compared to PCDD/PCDF is the higher vapour pressure, as table 3 shows. Therefore different tests at temperatures 40°C, 50°C and 60°C were performed.

Table 3: vapour pressure[3)]		Table 4: applied standard mixture
[Pascal]	25°C	1 µg naphtalene
OCDD	1,1E-10	1 µg acenaphtylene
1,2,3,4,7,8-H_6CDD	5,1E-09	1 µg benz[a]pyrene
2,3,7,8-T4CDD	2,0E-07	1 µg benzo[g,h,i]perylene
PCB 153	1,3E-04	1 µg 2`,4,5 T_3CB
PCB 101		1 µg 2,2′,3,4,5 T_5CB
PCB 29	1,3E-02	1 µg 2,2′,4,4′,5,6 H_6CB

The investigation was carried out on the DMS fliterunit, which is in principle a glass fibre filter/PUR/PUR sampling train. The glass fibre filter has a surface area of 0.1 m², the PUR-foams have an diameter of 0.08 m (0.05 m thick). Before every test a standard mixture, as described in table 4 was applicated to the glass fibre filter.

Test runs were performed by sucking 100 m³ air through this sampling train (5 m³/hr) at temperatures of 40°C, 50°C, 60°C. Afterwards the concentrations in each part (GF-filter, 1st PUR, 2nd PUR) were determined.

7. Results

Table 5: results at 40°C as an example:				
	GF-Filter	1st PU	2nd PU	break-trough
	[%]	[%]	[%]	[%]
naphtalene	36.4	55.0	7.5	1.2
acenaphtylene	24.4	49.4	17.1	8.5
benz[a]pyrene	29,.0	23.2	17.4	30.5
benzo[g,h,i]perylene	97.3	2.7	0.0	0.0
2',4,5 T_3CB	1.2	68.4	21.2	9.3
2,2',3,4,5 P_5CB	1.6	98.4	0.0	0.0
2,2',4,4',5,6' H_6CB	17.6	82.4	0.0	0.0

8. Conclusion

It is known, that the the monitoring and surveillance system DMS can be used for permanent monitoring and for short-term measurements of PCDD/F. As the results of this work showed, the operating field of such a system can be expanded to a much wider range of organic compounts.

As the results of table 5 shows, PUF-foam has a very high absorbtion efficiency especially for the higher volatile PAHs naphtalene and acenaphtene, the first PUF-foam has a sufficient absorbtion efficiency for higher chlorinated biphenyls.

9. References

1) Lützke K., Patentschrift DE 31 36 646, 1983

2) Kahr G, Dioxin 94, Innovations in permanent monitoring of PCDD/F from a hazardous waste incinerator

3) Ericson M., Analytical Chemistry of PCBs, 1992 by Lewis Publishers