

SIMULTANEOUS SAMPLING AND DETERMINATION OF POLYCHLORINATED BIPHENYLS, HCB AND PCDD/PCDFs IN STACK GASES

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Introduction.

Polychlorinated biphenyls (PCBs) were widely used in the past for as an additive for mineral oils used in electrical equipment, heat exchangers, as well as plasticizers. They are highly resistant to biological and chemical degradation. Therefore, they persist in the environment for many years^{1,2}. Among the all of PCB congeners there are 12 so called "dioxin-like" PCBs, recognized as highly toxic compounds^{3,4}, however they are not commonly analysed in stack gases as dioxins. There are no requirements concerning their maximum allowable concentration in stack gases. Stockholm Convention require for example monitoring and reporting emission data for unintentionally released POPs as dioxins, PCB and HCB. Although there is an established EU standard for the determination of PCDD and PCDF concentration in stack gas from waste incineration (European Standard EN-1948:1996⁵), this standard is not validated yet for the determination of PCB and HCB. Therefore, the sampling methodology used in this work was developed at Krakow University of Technology because of the complexity of PCDFs, PCDDs, PCB and HCB simultaneously sampling and determination.

In this work the sampling train, based on filter/condenser method as it is described in European Standard EN-1948:1996 part 1 was used. In this work average of 10 Nm³ samples were taken for simultaneous determination of PCBs, PCDD and PCDF, and HCB in the stack gases. The sampling methodology and equipment use in this work was developed at Technical University of Krakow, with using sampling apparatus – EMIOTEST 2598 (Poland, Wrocław). The procedures guarantees 90-95% collection efficiency of PCDDs, PCDFs, PCBs and HCB from flue gas. The validation tests were performed on iron ore sinter plant (Mittal Steel, Cracow, Poland) using two PU-foam plugs connected in series. In the second adsorbent – PU foam – the break-through masses of individual congeners were determined.

Materials and method.

The main aim of this research was checking the ability to simultaneous sampling and determination of PCDDs, PCDFs, 12 WHO Dioxin-like PCBs, 6 Indicator PCBs and HCB in stack gases. The validation tests were performed on iron ore sinter plant in 4 series with using two PUF (polyurethane foam) serial – one by one. In the second PUF break-through masses of analysed contaminants were checked.

The four independent measures were performed:

1. 15.07.2005 between 9:30 – 14:00. 12.30 Nm³ wet gas, operational O₂
2. 15.07.2005 between 15:00 – 20:15. 11.10 Nm³ wet gas, operational O₂
3. 20.07.2005 between 8:15 – 14:30. 9.55 Nm³ wet gas, operational O₂
4. 20.07.2005 between 15:45 – 21:45. 10.25 Nm³ wet gas, operational O₂

Sinter plant was operated at standard conditions and stack gas parameters were stable, however due to the technological requirements, some input materials varied in compositions, especially iron ore composition.

The schematic presentation of the apparatus is presented in **Fig.1**. This instrument was specially designed at our university for isokinetic sampling of industrial gas samples for the determination of trace organic compounds and is validated for the determination of PCDD, PCDF, PCB and HCB.

Sample preparation and analysis

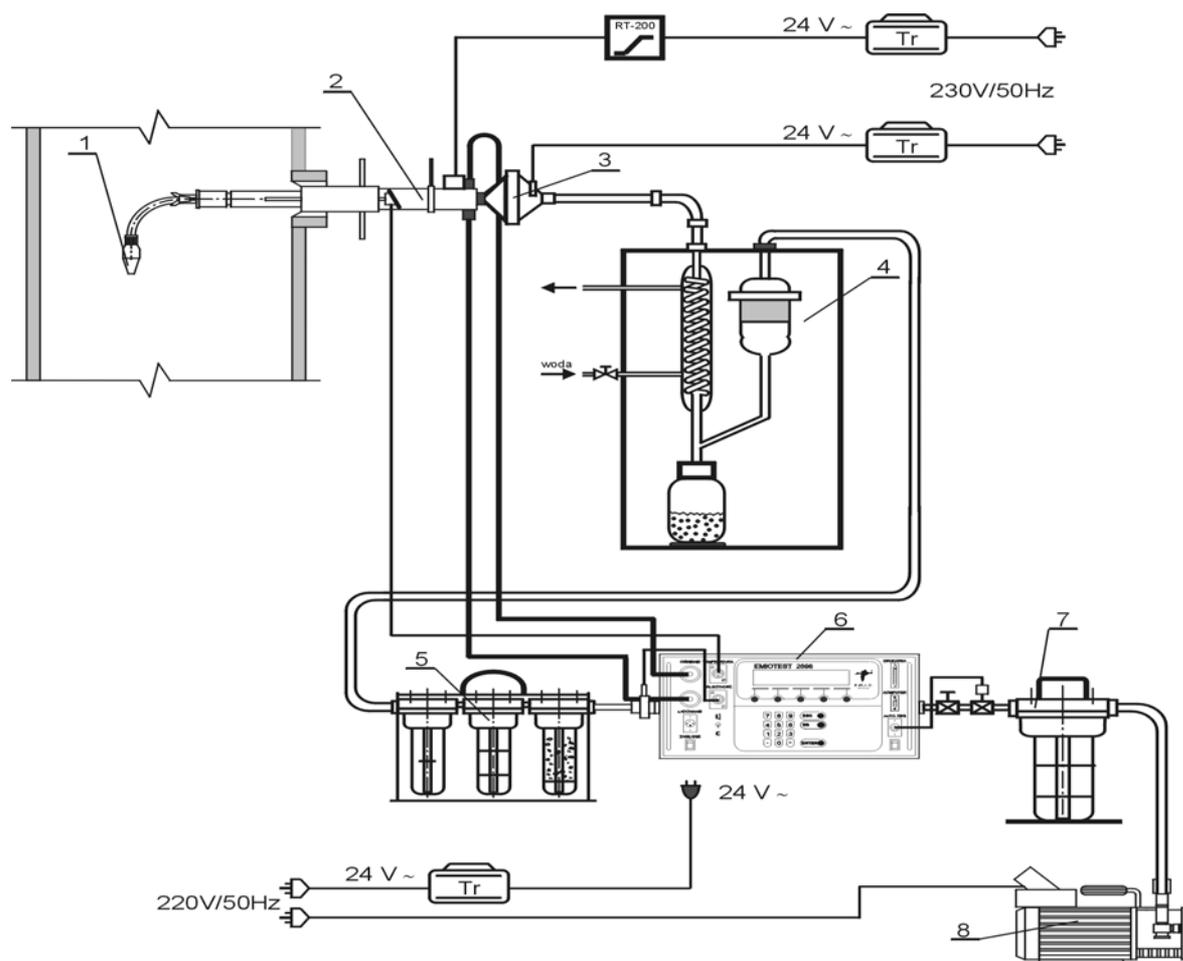


Fig. 1: Sampling apparatus used in the determination of breakthrough of PCDD, PCDF, PCB and HCB in Krakow Mittal Steel Works from the emission from iron ore Sinter plant stack. On the fig.1 only one (PUF-1) cartridge – No:4 is presented.

In this experiment, subsequential, the second one (PUF-2) was mounted.

Sampling nozzles (1) and probe (2) were made of titanium (1). Fly ash (if present) were taken using glass fibre filters of pore size of $0,2 \mu\text{m}$ which were placed in the heated compartment (3). For stack gas or off-gas of high humidity an aqueous condensate containing dissolved compounds was collected. PCDD, PCDF, PCB and HCB present in vapour form in cooled flue gas stream were adsorbed on PU-foam plug placed in a cartridge (4). In this work the product No: 20038 obtained from "Supelco", Bellefonte, USA was used.

Samples gas was dried with silica (5) and gas volume, humidity, temperature and pressure were recorded in central unit (6). Pulse damper (7) is used for stabilizing of sampling gas pump operation (8).

All compartments before sampling were spiked with appropriate ^{13}C PCDD/F, PCB and HCB sampling standards for sampling recovery control.

Samples of fly ash collected on glass fibre filters, PU-foam and water condensate were immediately delivered to the laboratory. After standard addition samples were extracted with toluene according to procedures recommended by EN-1948. After extraction, Semipermeable Membranes technique, column chromatography with using silica gel and acidic/basic alumina for clean-up were used. PCDD, PCDF, PCBs and HCB in the extracts were determined by gas chromatography coupled with mass spectrometry detection, with multistep fragmentation of molecules – GC-MS/MS.

Sample preparation and analysis

Result and Discussion

In this work we obtained 90-95% collection efficiency of PCDDs/Fs, PCBs and HCB from flue gas. Limit of Detection (LD) for PCDDs/Fs and PCBs, calculated for stack gas samples was 0.002 – 0.005 ng I-TEQ/Nm³. LD for HCB was in the range of 0.05 – 0.1 ng/Nm³

The validation tests performed on iron ore sinter plant (Mittal Steel, Krakow, Poland) in June 2005 have shown that the average break-through mass of PCBs and HCB is not higher than 10% of total mass of measured congeners in the measured stream of sampling gas. The average break-through mass of PCDDs/PCDFs is lower than 1% of total mass of 17 congeners. Validation was performed using two PU-foam plugs connected in series and the break-through masses of individual congeners were determined in the second adsorbent.

Tab.1. Contents of PCDDs, PCDFs, 12 WHO Dioxin-like PCBs, 6 Indicator PCBs and HCB in for samples from the emission from iron ore Sinter plant stack. (Total mass = fly ash on filter + condensate + PUF-1 + PUF-2)

Sample No.	Total mass HCB ng/m ³	Total mass I-PCB ng/m ³	Total mass WHO PCBs ng/m ³	Total mass PCDDs/Fs ng/m ³	Total mass WHO PCBs ng-TEQ/m ³	Total mass PCDDs/Fs ng-TEQ/m ³
1	224.5	331.8	28.8	20.9	0.115	1.171
2	365.0	409.9	32.6	23.8	0.203	1.507
3	217.3	203.2	21.0	42.4	0.050	2.315
4	405.0	641.9	45.1	46.8	0.097	2.544

Data in the Table 1 shown very similar contents of particular group of trace organic compounds, with using glass fibre filter and PU-foam as an adsorbent. To check the sampling efficiency and the analyte breakthrough for PCDDs/Fs and especially for PCBs and HCB, in this work two PU-foam plugs connected in series were used. Results of break-through values with respect to the mass adsorbed on PUF-2, for PCDDs/Fs, PCBs and HCB are presented in tables 2A, 2B, 2C, and 2D.

Tab. 2A. Break-through values of D-L PCBs with respect to the mass adsorbed on PUF-2

Sample	% Break-through Dioxin-like PCBs PUF-2/ Total mass	% Break-through Dioxin-like PCBs PUF-2/ PUF-1
1	8.3	9.6
2	6.5	9.0
3	9.2	10.0
4	5.9	7.5
Average	7.5	9.0

Tab. 2B. Break-through values of I-PCBs with respect to the mass adsorbed on PUF-2

Sample	% Break-through Indicators PCBs PUF-2/ Total mass	% Break-through Indicators PCBs PUF-2/ PUF-1
1	8.7	9.2
2	7.5	9.6
3	10.6	13.3
4	5.0	7.2
Average	8.0	9.8

Tab. 2C. Break-through values of PCDDs/Fs with respect to the mass adsorbed on PUF-2

Sample	% Break-through Dioxin-like PCBs PUF-2/ Total mass	% Break-through Dioxin-like PCBs PUF-2/ PUF-1
1	1.0	9.3
2	0.7	4.7
3	0.3	6.1
4	0.3	3.8
Average	0.6	6.0

Tab. 2D. Break-through values of HCB with respect to the mass adsorbed on PUF-2

Sample	% Break-through Indicators PCBs PUF-2/ Total mass	% Break-through Indicators PCBs PUF-2/ PUF-1
1	3.6	9.4
2	4.8	15.4
3	3.6	10.7
4	2.4	10.3
Average	3.6	11.5

Explanations:

% Break-through PUF-2/Total mass is calculated as: PUF-2 / TOTAL MASS * 100%

% Break-through PUF-2/PUF-1 is calculated as: PUF-2 / (PUF-1 + PUF-2) * 100%

Sample preparation and analysis

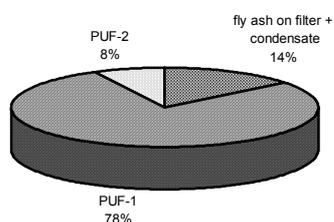


Fig. 2A. Average contents of D-L PCBs in adsorbents.

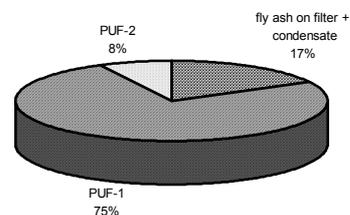


Fig. 2B. Average contents of I-PCBs in adsorbents.

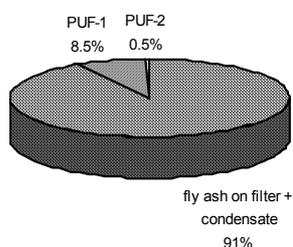


Fig. 2C. Average contents of PCDDs/Fs in adsorbents.

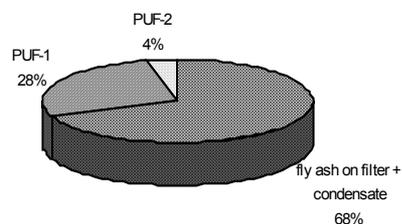


Fig. 2D. Average contents of HCB in adsorbents.

The result from this work indicates, that this method, is suitable for simultaneous sampling and determination of polychlorinated biphenyls, PCDDs/PCDFs and HCB in stack gases from thermal processes as metallurgical sectors, power generation, incineration of municipal and hazardous wastes and others. The apparatus used in this work is also suitable for the simultaneous sampling of PAHs and heavy metals.

References

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