

**SIMULTANEOUS SAMPLING OF PCDDS AND PCDFS
AT THE MWI SPITTELAU / VIENNA**

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ABSTRACT

Since several countries have released statutory emission limits for PCDDs and PCDFs in the range of 0.1 ng 2,3,7,8-TCDD TE/Sm³, reliable sampling and analytical procedures must be established in order to guarantee reproducible results. The extraction, clean-up and analytical procedure are nowadays considered to be no longer a major source of errors, but much larger uncertainties are related to non-representative sample collection, the possibility of artefacts resulting in discrepant results and eventually small recoveries. In order to assess the intralaboratory deviation of the sampling and analytical method under field conditions six simultaneous samplings were performed. In addition a long term sampling over a period of 11-day period was carried out, in order to test the representativity of regular samplings.

EXPERIMENTAL

The investigations were carried out at the municipal waste incinerator Spittelau/Vienna. The plant receives solid municipal waste (250.000 t/year), including non-infectious municipal-like hospital waste (1 %). This MWI is designed in two units, each receiving 16 t/h with H_U at 9200 KJ/kg. The flue gas treatment system is composed of an electrostatic precipitator, a two-stage wet scrubber followed by a wet electrodynamic venturi and as the final flue gas treating device for both lines a common "tail end"-type SCR-unit.

The SCR-Box is composed of two units installed in 1989, and a third unit which was added in 1991 (17,000 operating hours by April 1993). The NH₃-injection-device is placed

upstream of the heat-pipe, which raises the flue gas temperature from 100 to 220°C. A duct burner unit is needed to reach the operation temperature of 280°C. Temperature after the heat-pipe is 160°C and 117°C in the stack. The catalyst has a honeycomb form and consists primarily of V₂O₅ and WO₃ supported on a TiO₂-carrier (pitch 4 mm). Average gas flow was 100,000 Sm³/h per line in each test run.

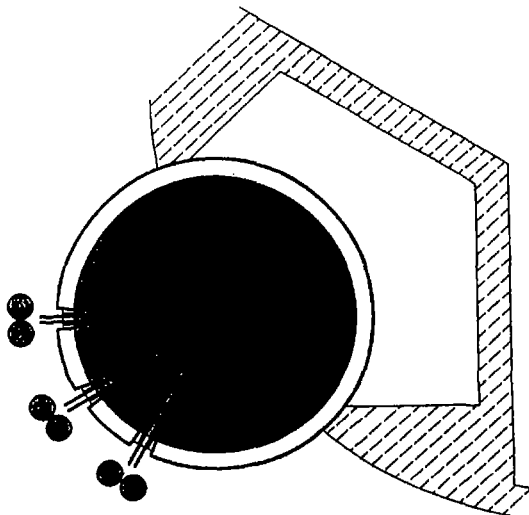
Sampling

Three test runs were performed within a 2 weeks period, test-run # 3 consisting of six simultaneous samplings within one day, while test-run # 2 was performed over an interval of 11 days with one day interruption due to a mechanical problem at the stoker grade. In addition test-run # 1 was carried out at the beginning of the long-term-sampling.

The combustion and flue gas cleaning system conditions were similar in all performances. The PCDD/PCDF-samplings of test runs 1 and 3 were carried out over approximately 6 hours by means of the sampling train recommended by the "Schweizer Bundesamt für Umweltschutz" and LAGA 11.172, as described in a former publication (1). 1,2,3,4-TCDD was used as sampling spike and the volumes collected were about 10 Sm³. The long-term-sampling was carried out at three points in the gas-stream and the total sampling volume was in the order of 380 Sm³.

All the samplings were made at the same location in the stack using different sampling ports (Fig.1).

Fig. 1: Schematic sketch of the sampling ports



CLEAN-UP AND HIGH-RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Details of the clean-up procedure used and the GC/MS-analysis were reported elsewhere (1). Identification and quantification was carried out by monitoring two masses ($[M]^+$ and $[M+2]^+$, eventually $[M+2-COCl]^+$ and $[M+4]^+$), and comparing the peak areas of the native isomers with the areas of the corresponding isotope labeled internal standards, assuming the same response for labeled and unlabeled isomers. Positive identification was made when the following criteria were fulfilled: correct retention time (± 3 sec), signal-to-noise ratio $> 3:1$, and correct isotope ratio ($\pm 15\%$). Recovery rates of the added ^{13}C -marked congeners should be $> 50\%$.

RESULTS

Table 1 present the levels of PCDD/PCDFs measured at the sampling ports during the test runs. They are quoted in ng per standard cubic meters ($0^{\circ}C$, 101,3 kPa, dry gas, 11% O_2) as noted by ng/Sm^3 . 2,3,7,8-tetrachlorodibenzo-p-dioxin Toxic Equivalent (TEQ) were

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calculated using the NATO/CCMS-factors. In case of undetectable levels, the congeners were not included in the computation.

The PCDD/F-levels of test run #3 expressed as TEQ-values fluctuate between 0.034 and 0.042 ng/Sm³, giving an average value of 0.041. These values are in good agreement with previous measurements (2). The estimates of reproducibility expressed as standard deviations (RSD) are as follows:

SD	0.0057 ng TEQ (I-TEF)/Sm ³	RSD	13.90 %
SD	0.2566 ng/Sm ³	RSD	15.50 %

Tab.1: Summary of PCDD and PCDF data for all samples, ng TEQ (I-TEF)/Sm³

		ng/Sm ³	ng TEQ/Sm ³
Test # 1	19.01.93	1.983	0.035
Test # 2	19.01.93- 29.01.93	1.462	0.034
Test# 3	sample B1	29.01.93	1.911
	sample B2	29.01.93	1.879
	sample C1	29.01.93	1.711
	sample C2	29.01.93	1.359
	sample E1	29.01.93	1.757
	sample E2	29.01.93	1.320

REFERENCES

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2. R.Boos, R.Budin, H.Hartl, M.Stock and F.Wurst: PCDD- and PCDF- destruction by a SCR-Unit in a municipal Waste incinerator. Chemosphere Vol.25, No.3, pp 375-382 (1992).