

Comparison of Dioxin sampling methods; USA EPA method 23 versus two German VDI methods

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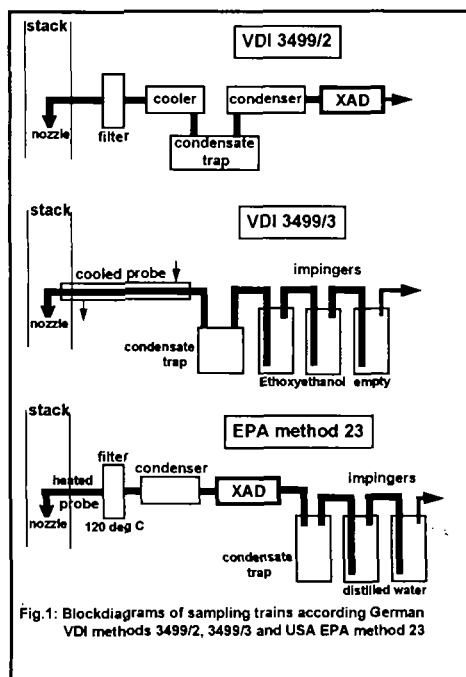
Introduction

An intensive evaluation and research program has been in progress for three years at the Stade (Germany) site of The Dow Chemical Company. This evaluation and research is directed towards meeting the German legislation on waste incinerator emissions. On the Stade site a wide range of gaseous, liquid and solid residues and wastes need to be treated for recycle and disposal. The Chlorine content of these materials ranges from < 0.1% to 80%. A rotary kiln serves as central unit for disposal of all solid materials and some smaller incinerators (TTU's; thermal treatment units) incinerate liquids

and vent gases only. The hydrochloric acid from the combustion processes is recovered as a product and/or utilized internally as a raw material for other processes.

The research program to optimize the operation of the kiln and TTU's is on schedule for compliance with the new regulations in Dec 1996. The studies were focused on optimization of burner operation and control, on measures to reduce the reformation potential and on some selected end-of-the-pipe catalytic post treatment techniques. Approximately 100 PCDD/PCDF numbers were generated during that program reflecting different modes of operation and different test runs. Two out of four German VDI methods were used. VDI 3499/2¹⁾ (fig. 1) was applied by certified outside institutes for compliance measurements and for cross checks with VDI 3499/3²⁾ (fig. 1). This latter method was chosen for internal sampling campaigns. Extraction, clean up and analyses were always done by external laboratories.

This sampling project was also initiated to validate the Stade site PCDD/PCDF data for



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comparison with USA data in general and for the use within the global Dow organization. To our knowledge no transcontinental comparison of PCDD/PCDF sampling techniques applied at industrial incinerators has been published so far.

Project scope and procedure

Two incinerators were chosen for the study to best represent the feed characteristics and the hardware components to achieve the objectives of the sampling project. The kiln and a heat recovery TTU provided the above criteria and are also similar to units that operate globally within Dow.

5 sampling runs were planned for the kiln:

- kiln-1: normal operation at full capacity / 2 hours sampling
- kiln-2: repetition of kiln-1
- kiln-3: normal operation at full capacity / 4 h sampling
- kiln-4: enhanced particle emissions ($> 15 \text{ mg/Nm}^3$) / 2 h sampling
- kiln-5: reduced PCDD/PCDF emission level / 2 h sampling

3 sampling runs at the TTU:

- TTU-1: normal operation at full capacity / 2 h sampling
- TTU-2: normal operation at full capacity / 4 h sampling
- TTU-3: without cocombustion of natural gas / 2 h sampling

All three sampling trains were operated simultaneously for the 2 respectively 4 hour runs. Two stages at different stack height were necessary to provide sufficient space for the three trains. At the kiln VDI 3499/3 and EPA method 23³⁾ were located on the lower level and at the TTU both sampled on the upper stage. VDI 3499/2 and EPA method 23 were conducted in full compliance with requirements to stack gas flow profile evaluation and to 90 degree traverse sampling. VDI 3499/3 used a simplified set up without traverse sampling and without any change of the nozzle location after the run was started. Each train was spiked with ¹³C standards according to its own procedure. The gas volumes taken were very similar for all trains and runs; 3 - 4 Nm³ for 2 h and ca. 7 Nm³ for 4 h.

Extraction, clean up and analysis were performed by three different laboratories. All samples taken by one train were always analyzed by the same laboratory. The inter-laboratory consistency and comparability was tested independent from this program and delivered no evidence for significant differences. Nevertheless all raw extracts were split for an optional analysis by one of the partner labs if any further questions would have occurred.

Following EPA method 23 the quantification of sum of PCDD and PCDF was not done. The 123478- and 123678-HxCDD respectively the 123478- and 123678-HxCDF were quantified as the sum of both isomers only. For comparability reasons the results were divided by 2 and assigned to the individual isomers in tab.2.

Results

Fig.2 shows the results of all 8 runs in ng ITE/Nm³. In all cases with exception of kiln-3 an identical pattern is observed. VDI 3499/2 is lower than EPA 23 by 1.6 to 42 % and VDI 3499/3 is with 21 to 57 % also always below EPA 23. Only for the 4 h sampling of kiln-3 VDI 3499/3 is higher than -/2. All different ratios are listed in tab.1 where the EPA 23 levels are set to 100%.

In comparison to the related kiln results the TTU averages are in general lower: 12% for VDI 3499/2 respectively 18% for VDI 3499/3. Except of this finding there are no further systematic differences for the VDI 3499/3 averages obvious. All VDI 3499/2 averages for 2 h sampling range from 71 to 89 % of EPA 23 levels. The two 4 h numbers are lower: 58 and 61 %.

	VDI 3499/2	VDI 3499/3	EPA method 23
average kiln 2h	89 %	64 %	100 %
kiln 4h	58 %	71 %	100 %
average all kiln	83 %	66 %	100 %
average TTU 2h	76 %	51 %	100 %
TTU 4h	61 %	43 %	100 %
average all TTU	71 %	48 %	100 %
average all 2h	85 %	59 %	100 %
average all 4h	59 %	57 %	100 %
average all runs	78 %	59 %	100 %

Tab.1: ITE levels of VDI 3499/2 and -/3 relative to EPA method 23

Tab.2 shows the normalized isomer distributions for runs kiln-1, kiln-2 and kiln-4. The lower numbers of VDI 3499/3 compared to EPA 23 result basically from general lower levels for all tetra through octa congeners and for both Dioxins and Furans. VDI 3499/2 shows in most runs a very acceptable agreements with EPA 23 for all isomers but a more random scattering with higher or lower values on both sides. The higher ITE results of EPA 23 versus VDI 3499/2 for the 4 hour runs are mainly caused by higher hepta and octa isomer levels.

The conspicuous deviation of the values for the 123789-HxCDF isomer within the VDI 3499/3 samples at kiln-2 and kiln-4 might be a result of an overlapping and co-elution of the 1234678-HpCDF due to a loss m/z 34 (-Cl +H) on the isomer specific GC-column.

MEASUREMENT sampling method	kiln-1			kiln-2			kiln-4		
	VDI 3499/2	VDI 3499/3	EPA method 23	VDI 3499/2	VDI 3499/3	EPA method 23	VDI 3499/2	VDI 3499/3	EPA method 23
ITE (11% O2/273 K)	0.376	0.194	0.382	0.393	0.296	0.459	0.393	0.349	0.441
ITE (7% O2/293 K)	0.490	0.253	0.498	0.512	0.386	0.598	0.515	0.455	0.575
ITE (O2 org.)	0.376	0.196	0.382	0.361	0.269	0.422	0.320	0.275	0.357
O2 sampling	11.00	10.90	11.00	11.80	11.90	11.80	12.87	13.10	12.90
Tetra-CDD, Sum	1.000	0.384	-	1.000	0.114	-	1.000	0.380	-
2.3.7.8TCDD	1.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
Penta-CDD, Sum	1.000	0.704	-	1.000	0.329	-	1.000	0.430	-
1.2.3.7.8 PeCDD	1.000	0.597	0.000	1.000	0.633	0.000	1.000	0.394	0.000
Hexa-CDD, Sum	1.000	0.601	-	1.000	0.550	-	1.000	0.500	-
1.2.3.4.7.8 HxCDD	1.000	0.000	1.795	1.000	0.000	1.636	1.000	0.000	2.286
1.2.3.6.7.8 HxCDD	1.000	0.000	1.068	1.000	0.000	0.947	1.000	0.000	1.185
1.2.3.7.8.9 HxCDD	1.000	0.000	1.150	1.000	0.000	1.348	1.000	0.000	1.400
Hepta-CDD, Sum	1.000	0.459	-	1.000	0.501	-	1.000	0.543	-
1.2.3.4.6.7.8 HpCDD	1.000	0.443	0.986	1.000	0.443	1.026	1.000	0.478	1.149
Octa-CDD, Sum	1.000	0.442	0.664	1.000	0.387	0.526	1.000	0.439	0.870
Tetra-CDF, Sum	1.000	0.219	-	1.000	0.415	-	1.000	0.383	-
2.3.7.8 TCDF	1.000	0.197	0.927	1.000	0.276	0.710	1.000	0.394	0.536
Penta-CDF, Sum	1.000	0.418	-	1.000	0.978	-	1.000	0.982	-
1.2.3.7.8 PCDF	1.000	0.597	0.709	1.000	1.182	1.213	1.000	0.698	1.013
2.3.4.7.8 PCDF	1.000	0.410	0.667	1.000	1.358	0.907	1.000	2.475	0.667
Hexa-CDF, Sum	1.000	0.590	-	1.000	0.611	-	1.000	0.742	-
1.2.3.4.7.8 HxCDF	1.000	0.710	0.945	1.000	0.521	1.162	1.000	0.570	0.935
1.2.3.6.7.8 HxCDF	1.000	0.698	1.050	1.000	0.384	1.310	1.000	0.643	0.987
1.2.3.7.8.9 HxCDF	1.000	0.000	1.045	1.000	15.852	1.462	1.000	11.237	0.974
2.3.4.6.7.8 HxCDF	1.000	0.314	1.081	1.000	0.365	1.402	1.000	0.285	1.290
Hepta-CDF, Sum	1.000	0.454	-	1.000	0.440	-	1.000	0.465	-
1.2.3.4.6.7.8 HpCDF	1.000	0.480	0.920	1.000	0.534	0.914	1.000	0.537	1.175
1.2.3.4.7.8.9 HpCDF	1.000	0.318	1.383	1.000	0.282	1.099	1.000	0.291	1.469
Octa-CDF, Sum	1.000	0.801	1.268	1.000	0.625	1.058	1.000	0.675	1.111

Tab.2: ITE results and normalized isomer comparison of runs kiln-1, kiln-2 and kiln-4.

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Conclusions

Because all the stack gas ITE concentrations collected and measured during this study fell in the range of approximately 0.1 to 0.6 ng ITE/Nm³, the results presented in fig.2 demonstrate excellent agreement between EPA 23 and VDI 3499/2, and reasonably good agreement between all three sampling trains and analytical methods. It is important to note that this study was conducted in the absence of any preliminary laboratory collaboration to confirm reference standard concentrations, or to test the reliability of simultaneous sampling of any given stack by three different probes all located at different points within the stacks that may have cyclonic flows.

Per data given in fig.2, EPA 23 sample collection and analysis procedure yields the highest PCDD/PCDF concentrations and VDI 3499/3 (with one exception) gives the lowest. Although these differences appear reproducible within this data set, in our opinion these differences are not significant, given the described constraints internal to the experimentation. Currently, continuing experimentation to isolate the 'apparent' systematic differences between US EPA and German sample collection and/or analysis procedure is beyond the scope of the project. What is important though, is the fact that either EPA 23 or VDI 3499/2 appear to yield comparable results when applied to the measurement of PCDD/PCDF in industrial TTUs when the analytes are present at concentrations at, or very near, 0.1 ng ITE/Nm³. In every case within this data set, excepting the 4 hour collection period sample (kiln-3), the final analyte concentrations can be detected and quantitated at 0.1 to 0.4 (+/- 0.1) ng ITE/Nm³.

References

- 1) VDI 3499, Blatt 2, Vorentwurf, Messen von Emissionen. Messen von polychlorierten Dibenzo-p-dioxinen (PCDD) und Dibenzofuranen (PCDF) in Abgasen industrieller Anlagen und Feuerungsanlagen mit Hilfe der Kondensationsmethode. Stand Juni 1990.
- 2) VDI 3499, Blatt 3, Vorentwurf, Messen von polychlorierten Dibenzo-p-dioxinen (PCDD) und Dibenzofuranen (PCDF) an industriellen Anlagen. Kondensationsmethode - gekühltes Absaugrohr. Stand Juni 1990.
- 3) Revision 0; April 1994; Draft copy for the new US EPA Method 23: Sampling method for polychlorinated Dibenzo-p-dioxin and polychlorinated Dibenzofuran emissions from stationary sources.

**Fig.2: Comparison of Dioxin sampling methods
USA EPA method 23 versus two German VDI methods**

