

MONITORING PCDD/F DE-NOVO SYNTHESIS IN A MUNICIPAL WASTE INCINERATOR

Stefano Raccanelli, Werner Tirlir*, Maurizio Favotto, Massimo Donegà*

Consorzio Interuniversitario Nazionale la Chimica per l'ambiente, V. della Libertà 5/12, 30175 Marghera (VE), Italy

*Eco-Center, V. Lungo Isarco Sinistro 57, 39100 Bolzano (BZ), Italy

Introduction

With the discovery of PCDD in emissions of municipal waste incinerators¹ also the question of their provenience came up. In the incineration process temperatures of about 1000 °C are normal for a few seconds. Under these conditions all organic compounds should be destroyed. If PCDD/F are still found in the flue gas, then they must be attributed to reformation process². As measurements proved³, conventional electro-filter working approximately 250 °C were responsible for this. Concentration of PCDD/F at the exit of the filters were much higher than at their entrance. Thus, actually a flue gas cleaning device has contributed to high emission levels. After this discovery incineration was labeled as dangerous environmental polluter and waste incineration is still seen sceptically. However modern incineration plants hardly contribute to the total emission compared to the other sources^{4, 5} (industry, traffic, etc.). The average domestic waste contains about 50 ng/Kg⁶. Emitting this amount completely by flue gas you would find about 10 ng/Nm³ in the emissions. Modern incinerators are emitting below 0,1 ng/Nm³ (European Limit) and so they actually do remove dioxins. Such low emission levels were possible to realize also because the mechanism of the de-novo synthesis were investigated and so countermeasures could be taken. Just by lowering the filter temperature could be reduced. Further investigation revealed that temperatures at about 300 °C maximised reformation of PCDD/F. Recently another reformation maximum, mostly for PCDF, at approximately 450 °C was found⁷. This study reports the results of an investigation which was carried out in a municipal waste incinerator which has been active already since several years.

Materials and Methods:

Procedure. All glassware was washed with basic detergent, rinsed with distilled water, treated with a solution of ammonium persulphate 350 g/L in sulphuric acid (98%) and rinsed twice with distilled water and acetone. Subsequently, the cleaned glassware was treated with dimethyldichlorosilane 5% in toluene, rinsed twice with distilled water and acetone, heated to 300°C for 3h, and covered with aluminium foil. Clean up. The sample extracts were treated with sulphuric acid (98%) and potassium hydroxide (20%) in a 100 mL separatory funnel and then cleaned up using the automatic three column system, Dioxin Prep (Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica, alumina and carbon were used. **Analysis.** The HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Sample injections were performed in the splitless mode on a 60 m Rtx 5 ms column (Restek 0.25 mm ID, 0.25 µm film) and on a 30 m Rtx 200 one (Restek 0.25 mm ID, 0.25 µm film) for verification. The analytical system was calibrated by calibration standard CS1 through CS5 (EDF-9999 Cambridge Isotope Laboratories Inc. CIL).

Formation and Sources P145

Sampling: was performed at the exit of the boiler and at the entrance of the fabric filter (after superheater and economiser). Sampling at the exit of the boiler was rather difficult; the conditions mentioned in EN 1948⁸ could hardly be followed because dust concentration were nearly 5 g/Nm³ and temperatures close to 500 °C. The following variant of the filter-cooler method was employed: the sampling tube was cooled by water to avoid artefacts, whereas the flue gas was not cooled below the dew point of water, because otherwise the condensing water could have damaged the filter by clogging it with the sampled dust. A condenser cooled by a mixture of glycol and water was set at the outlet of the filter and finally the sampled gas passed a methoxyethanol filled impinger. All the glassware, including quartz tubes were sylanized, such that almost all of the dust would remain in the dust-filter and not stick to the glass-surfaces. The flue gas temperature of the second sampling point in front of the fabric filter of the plant was only 220 °C. In this case sampling was done according to the filter cooler method with an external filter held at about 110 °C. Working conditions were not ideal, so during the preparation of this sampling many glass tubes were broken. Therefore a short piece of a not sylanized glass tube had to be used. At the end of the work the internal glass surface of this piece was covered by dust and looked like a neon tube, whereas the other tubes remained transparent.

Table 1

CONGENER	I-TEF	Exit Boiler			Filter Entrance		
		particulate phase	gas phase	Total (particulate + gas phase)	particulate phase	Gas phase	Total (particulate + gas phase)
		pg			pg		
2378 TCDD	1	3,1	6,3	9,4	21,4	50,3	71,7
12378 PCDD	0.5	4,3	11,9	16,2	27,5	107,5	135,0
123478 HxCDD	0.1	2,7	6,8	9,5	11,7	39,5	51,2
123678 HxCDD	0.1	4,1	8,0	12,2	15,9	43,5	59,4
123789 HxCDD	0.1	7,4	10,2	17,6	27,4	83,8	111,1
1234678 HpCDD	0.01	36,5	50,9	87,4	114,5	155,9	270,3
OCDD	0.001	161,0	149,6	310,6	336,9	384,6	721,4
2378 TCDF	0.1	19,9	27,4	47,2	68,2	146,2	214,4
12378 PCDF	0.05	20,2	54,0	74,3	107,4	346,5	453,9
23478 PCDF	0.5	12,1	20,0	32,1	37,2	268,0	305,2
123478 HxCDF	0.1	23,7	66,3	90,0	83,6	352,3	435,9
123678 HxCDF	0.1	14,3	39,1	53,4	58,3	226,2	284,5
234678 HxCDF	0.1	17,0	35,6	52,6	39,0	157,6	196,6
123789 HxCDF	0.1	2,8	9,2	12,0	8,2	33,2	41,4
1234678 HpCDF	0.01	44,1	101,5	145,6	110,9	510,2	621,1
1234789 HpCDF	0.01	10,7	20,2	31,0	18,9	63,0	81,8
OCDF	0.001	39,7	58,7	98,3	59,0	169,2	228,2

Results and Discussion

Only the toxicologically more relevant 2,3,7,8 congeners were evaluated in consideration. Gas phase and particulate phase were sampled and analysed individually. The two points of sampling were the exit of the boiler and the entrance of the fabric filter. Exactly the same sample volume was taken in the two points.

In Table 1 the contribution of the gas phase and particulate phase is shown separately as pg. Further the sum of gas phase and particulate phase is stated. Comparing the first point of sampling (exit of the boiler at 495 °C) to the second one (entrance of the filter at 220 °C) the rising concentration is clearly recognisable.

Table 2 states how many percents the concentration of the various 2,3,7,8 substituted congeners increases with the de-novo synthesis.

Generally one can see that in the particulate phase dioxins increase more than furans. In the gas phase this trend is less recognisable. However there is one which increased most of all: 2,3,4,7,8 PCDF – although being a furan – more than 900 %. The interesting point is, that exactly those three congeners (2,3,7,8 TCDD, 1,2,3,7,8 PCDD and 2,3,4,7,8 PCDF) with the highest I-TE factors increase most.

Further investigation are in progress.

Table 2

			Particulate Phase	Gas Phase	Total (Particulate +Gas)
CONGENERS	I-TEF		Increase in % (from boiler to fabric filter)	Increase in % (from boiler to fabric filter)	Increase in % (from boiler to fabric filter)
			%	%	%
2378 TCDD	1		681	802	762
12378 PCDD	0.5		638	904	833
123478 HxCDD	0.1		428	581	537
123678 HxCDD	0.1		382	543	488
123789 HxCDD	0.1		368	821	630
1234678 HpCDD	0.01		313	306	309
OCDD	0.001		209	257	232
2378 TCDF	0.1		343	535	454
12378 PCDF	0.05		530	642	611
23478 PCDF	0.5		309	1337	951
123478 HxCDF	0.1		353	531	484
123678 HxCDF	0.1		407	579	533
234678 HxCDF	0.1		230	443	374
123789 HxCDF	0.1		291	361	345
1234678 HpCDF	0.01		251	503	427
1234789 HpCDF	0.01		176	311	264
OCDF	0.001		149	289	232

Reference:

1. Olie K., Vermeulen P.L., Hutzinger O.; *Chemosphere*, **1977**, 6, 454.
2. Vogg H., Stieglitz L.; *Chemosphere*, **1986**, 15, 1373.
3. Vogg H.; *Organohalogen Compounds*, **1991**, 6, 279.
4. Rappe C.; *Fresenius J. Anal. Chem.*, **1994**, 348, 63.
5. Quaß U. and Fermann M.; The European Dioxin Inventory, **1997**, ISSN 0947-5206.
6. Vogg H.; *Z. Umweltchem. Ökotox.*, **1994**, 6, 367.
7. Schwarz G., Stieglitz L., Roth W.; *Organohalogen Compounds*, **1990**, 3, 169.
8. CEN, Stationary source emissions-determination of the mass concentration of PCDFs. Reports EN 1948-1,2 and 3, CEN **1996**