Assessment on dioxin, furan and DL-PCBs emissions in a hazardous waste incineration plant in Tarragona by using a long-term sampling equipment

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Introduction

The emission of hazardous substances to the atmosphere as by-products from incineration processes as well as from other industrial activities such as sinter plants, cement plants, etc are of great concern nowadays. Directive 2000/76/EC[1] of the European Parliament on the incineration of waste states that NO_x, CO, total particles, COT, HCl, HF, and SO_2 have to be monitored continuously since the appropriate techniques for this type of monitoring exist. In the case of organic compounds, particularly dioxins, the European Standard EN1948:2007 establishes 6 to 8 hour sampling period twice a year. In this regard, two measurements per year do not allows to determine the real contaminant emission rate. Therefore the determination on an emission factor coul be questionned strongly.

Continuous monitoring of organic contaminants such as PCDD/Fs and DL-PCBs is essential to know the real emission from a particular plant since this methodology allows to sample up to 6 weeks continuously. In this way, an accurate surveillance of the contaminants emitted to the atmosphere could be carried out since the samples collected are much more representative and as a consequence a precise assessment of the potential impact on the environment can be done.

In this work the results of a dioxin monitoring program using a continuous sampling system in a hazardous waste incineration plant are presented. The plant is located near Tarragona, in 50km^2 industrial area including chemical and petrochemical plants, as well as a municipal waste incinerator. It is the only hazardous waste incineration plant in Spain, equipped with one rotary killn operating at 1200ºC. The plant treats 30.000 t/y of halogenated and non-halogenated industrial waste, and results in a production of 25.000 kWh/year. Air pollution control system consists on an electrostatic precipitator followed by a humid scrubber, the addition of activated carbon and catalysts to treat 43.800m^3/h of flue gas. This study shows the first data using such monitoring system obtained in Spain.

Materials and Methods

Sampling process was carried out by using the long-term sampler DioxinMonitoringSystem® (MonitoringSystems, Wien, Austria) with the aim to collect PCDD/Fs and DL-PCBs. The principle of this system has been described in several publications[2]. Briefly, the sampling is based on the dilution method proposed in EN1948:2007 Part 1. The flue gas is isokinetically pumped by the alternate use of 2 probes to a thermostatic mixing chamber, where the gas is mixed with purified dry air to get a temperature of 40ºC. In addition the system provides continuous data on humidity content of sampled gas. Moreover, oxygen is also considered in order to normalize the gas volume.
Diluted gases passes through a cartridge containing firstly a particle filter followed by a 2-layer polyurethane foam (PUF). Sampling episodes were carried out in a monthly basis, resulting in an average volume of aproximately 300 Nm^3 of flue gas sampled. The whole process was controlled by the addition of standard solutions containing a mixture formed by both ^{13}C-PCDD/F and ^{13}C-DL-PCBs.

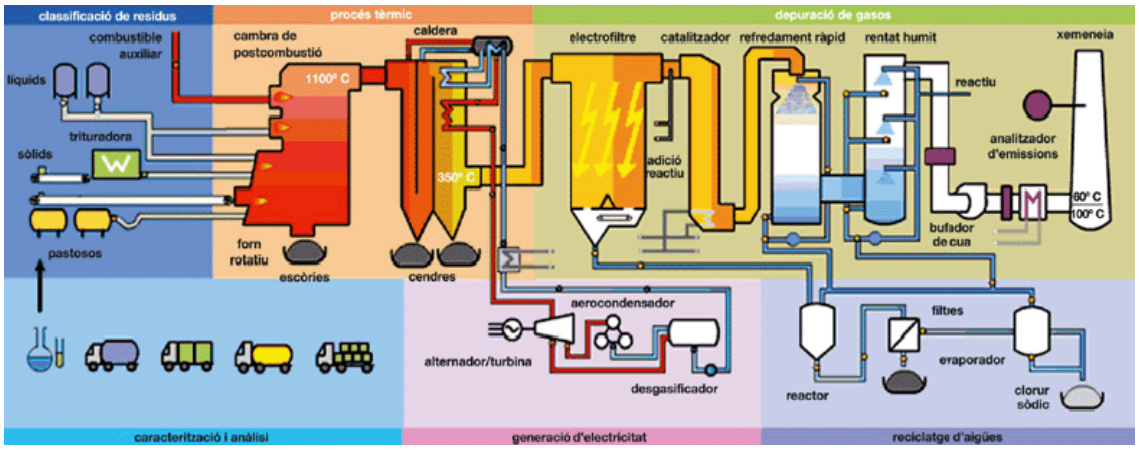


Fig.1. Configuration of the HWI plant of Tarragona

Once the cartridges were received at the laboratory, the polyurethane foams and the filter were spiked with known amount of a 13 ^{13}C- PCDD/F mixture (EN-1948-ES, Wellington Laboratories, Canada) and 12 ^{13}C- DL-PCBs mixture (P48-W-ES, Wellington Laboratories, Canada). After 2 hours, spiked samples were soxhlet extracted with toluene for 48h.

Clean-up procedure consists on solid-liquid adsorption chromatography based on a sequential array of the three different Teflon prepacked columns: multilayer silica, alumina and PX-21 carbon adsorbents, respectively (FMS Inc, Boston, USA) collecting the DL-PCBs and PCDD/Fs in separated fractions[3]. Instrumental analysis of PCDD/F analyses were performed on a gas chromatograph (Agilent 6890N, USA) fitted with a DB-5ms (60m x 0.25 mm i.d. x 0.25µm film thickness) fused silica column (J&W Scientific, CA, USA) coupled to a high resolution mass spectrometer (Waters, AutoSpec Ultima NT) operating in SIM mode at 10 000 resolving power (10% valley definition) and using the isotopic dilution as the quantification method. DL-PCBs were similarly analyzed despite that for this case a DB-XLB fused silica column (60m x 0.25 mm i.d. x 0.25 µm film thickness) from J&W Scientific was used.

Results and discussion

Table 1 summarizes the results obtained over 7 sample periods, expressed in both concentration (ng/Nm^3) and I-TEQ concentration (ng I-TEQ/Nm^3). The sampling period covers an average of 93% of the total time, due to stopping time. The results ranged between 0,007 and 0,036 ng I-TEQ/Nm^3, far below from the set limit of 0,1 ng I-TEQ/Nm^3. Recovery rates for sampling and analysis fulfilled the minimum requirements described in Standard EN1948:2007. Complementarly, finger print was also evaluated. Congener-specific distribution presented high similarity in all cases. As an example, Figure 2 represents a typical distribution.

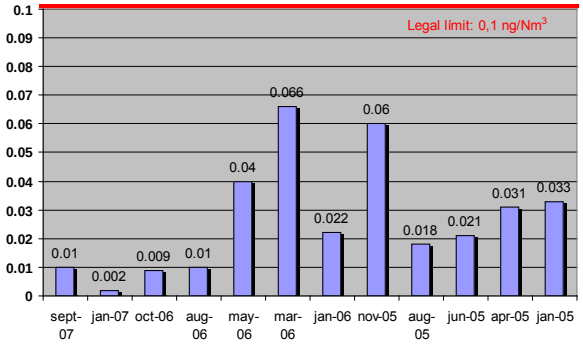
Fig 2. Congener-specific profile obtained in 1 month sample 1 month

	484/2007-EX	503/2007-EX	619/2007-EX	714/2007-EX	806/2007-EX	091/2008-EX	171/2008-EX
(pg/Nm^3)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
2,3,7,8-TCDF	0.009	0.011	0.007	0.006	0.004	0.005	0.002
1,2,3,7,8-PeCDF	0.016	0.019	0.010	0.007	0.007	0.010	0.004
2,3,4,7,8-PeCDF	0.023	0.024	0.016	0.012	0.010	0.016	0.005
1,2,3,4,7,8-HxCDF	0.029	0.038	0.017	0.012	0.012	0.020	0.007
1,2,3,6,7,8-HxCDF	0.026	0.034	0.016	0.012	0.012	0.020	0.007
2,3,4,6,7,8-HxCDF	0.032	0.039	0.021	0.015	0.015	0.024	0.010
1,2,3,7,8,9-HxCDF	0.001	0.001	0.001	0.002	0.001	0.001	0.0003
1,2,3,4,6,7,8-HpCDF	0.088	0.109	0.058	0.035	0.038	0.079	0.027
1,2,3,4,7,8,9-HpCDF	0.005	0.006	0.004	0.002	0.002	0.004	0.002
OCDF	0.020	0.026	0.015	0.007	0.007	0.015	0.006
2,3,7,8-TCDD	0.001	0.001	0.001	0.001	0.001	0.001	0.0002
1,2,3,7,8-PeCDD	0.007	0.010	0.004	0.004	0.003	0.004	0.002
1,2,3,4,7,8-HxCDD	0.006	0.009	0.004	0.003	0.002	0.004	0.001
1,2,3,6,7,8-HxCDD	0.013	0.017	0.008	0.005	0.004	0.007	0.003
1,2,3,7,8,9-HxCDD	0.006	0.009	0.004	0.002	0.002	0.004	0.001
1,2,3,4,6,7,8-HpCDD	0.027	0.041	0.022	0.011	0.009	0.017	0.007
OCDD	0.021	0.037	0.026	0.010	0.008	0.018	0.008
TOTAL I-TEQ (pg/Nm^3)	**0.030**	**0.037**	**0.020**	**0.015**	**0.013**	**0.021**	**0.007**
Sampling recoveries (%)							
^{13}C-1,2,3,7,8-PeCDF	113	68	68	87	104	115	105
^{13}C-1,2,3,7,8,9-HxCDF	91	91	94	92	94	112	104
^{13}C-1,2,3,4,7,8,9-HpCDF	72	75	85	77	81	104	96
sampled flue gas (m3,nc,dry)	89.33	250.33	335.28	312.00	356.58	283.21	126.16
Period	24/07-01/08	01/08-14/09	14/09-17/10	17/10-16/11	16/11-19/12	19/12-23/01	23/01-26/02

Table 1. PCDD/PCDF concentrations (ng/Nm^3) in 7 sampling consecutive periods

In addition, achieved data was compared to short-term sampling collections. Statistics of 48 analysis collected from 8 hours sampling reveals average values around 0.034 ng I-TEQ/Nm^3. This is consistent with achieved data collected using continuous monitoring system where the average values after 7 sampling period was 0.021 ng I-TEQ/Nm^3.

Fig 3. Short-term sampling determinations (2005-2007)



As quality assessment a blank including corrugated particle filter and polyurethane foam were evaluated, with a result of 9,97 total pg I-TEQ (to compare, the average of levels obtained in emission measurements was in the order of 5.000 total pg I-TEQ). Also a re-extraction of sample 3 was realized, in wich 18.1 total pg I-TEQ where found (less than 0,3% of the dioxins found in first extraction) proving that extraction efficiency meets the european standard requirement.

References

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2. Steiner T. *Organohalogen compounds* 66 (2004):787-790
3. Abad E., Sauló J., Caixach J., Rivera J. *J. of Chromatography* A 2000; 893:383.