

Sampling device for PCDD/F sampling in high temperature raw gases

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Introduction

Within the work for the Research Project “Thermal processes with energy recovery for sludge and special wastes disposal” carried out with the Water Research Institute, our group studied the conditions that can favour the PCDD/F formation during the incineration steps, especially in the high temperature sections as the afterburning chamber and the heat exchanger, where reformation reaction are documented [1,2]

The sampling of PCDD/F can be affected by many errors, but they can increase dramatically during the sampling of raw gases before the abatement devices, where the temperature and the concentration of other pollutants is very high. It is widely recognised that after particulate abatement PCDD/Fs are distributed between vapour phase and fine particles [3], but before abatement the distribution is hardly affected by temperature and by particles dimensions. For this reason the PCDD/F sampling need isokinetic conditions, otherwise it can be not representative of the real distribution. Moreover, a temperature-controlled procedure is needed, in order to avoid PCDD/F De Novo synthesis along the sampling train due to the cooling of sampled gases. For this kind of problems a device for high temperature sampling of organic micropollutant was developed.

Experimental

The sampling device consists of three main sections, a sampling probe, a section for conditioning the raw gas temperature and a a section for collecting the micropollutants. Previous experiences carried out on different types of incinerators put in evidence that the widely used alloys or materials such as Hastelloy and Titanium cannot be employed for the realization of the probes, because they can crash for effect of halogenidric acids and high temperature (> 1100°C). Ceramic materials are known to be resistant to high temperature and corrosive compounds, but some problems can occur due to their fragility and the adsorption of the particulate matter containing the micropollutants onto the high porosity materials.

For this reason a ceramic probe made of alumina with a porosity equal to zero was built (Figure 1). This material assures the best performances among all the refractory materials. It

does not show adsorbing properties that can reduce the efficiency of sampling for the micropollutants object of the study. It is resistant to corrosive environment and protects the device from the high temperatures of exercise. The dimensions of the sampling probe are as follows: internal diameter: 12 mm; length 1200 mm; Laboratory tests simulating the hard sampling conditions (thermal stresses and chemical aggression) of the materials were carried out.

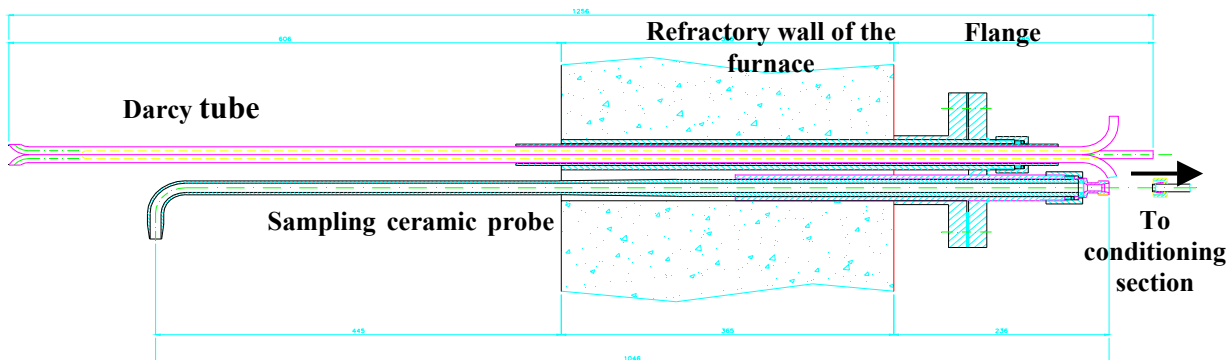


Fig. 1: Equipment for sampling in the afterburning chamber

The conditioning section must cool the raw gases temperature before they arrive in the filtering section, because the PCDD/F sampling must be carried out in a range of temperature above the water condensation temperature and under the range 250-400°C, in which the De Novo synthesis for PCDD/F could take place. For such considerations the gases must be lowered quickly to 110-140°C. The adopted device consists in a concentric tube exchanger in which the hot sampled gases are cooled down (Figure 2). The exchange surface is represented from a titanium tube, since this material is more acid resistant than stainless steel. The cold and hot fluxes have been set equicurrent for a better efficiency of the heat exchanger and because with this configuration the temperature of the out gases can be better controlled and the thermal stress is reduced. Moreover, the exchange surface can be increased, placing a second exchanger with a shorter section in series to the first one in order to maintain the speed of the warm fluid quite high, and consequently the thermal exchange coefficient. The dimensions of the exchange surfaces have been calculated in accordance with the cooling fluid and the incoming temperature. The length of the first and second exchange surface is 1200 mm and the diameter is 10 mm and 8 mm, respectively. The section for micropollutants collection is formed by a ceramic thimble filter where the heavier particles are collected and a XAD-2 resin, where the particles with smaller dimensions can accumulate. The filter is placed in a thermostatic section with a temperature above water condensation point (120-130 °C) and the XAD-2 resin (about 30 g) is placed in a cold thermostatic section (< 20 °C) (Figure 3 and 4). Finally, a section for condensed water is provided. This configuration allows to collect the major part of the condensables in the XAD-2

resin and to carry out a single solid-liquid extraction for the recovery of organic micropollutants.

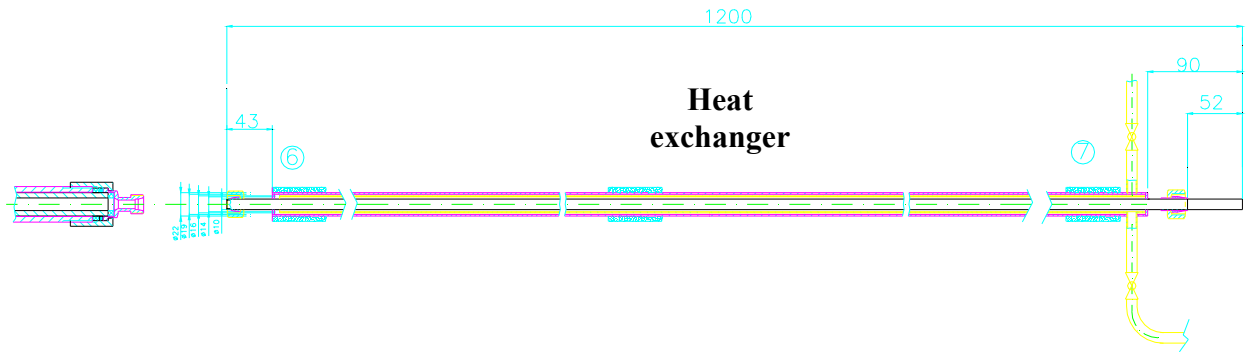


Fig. 2: Raw gas conditioning section

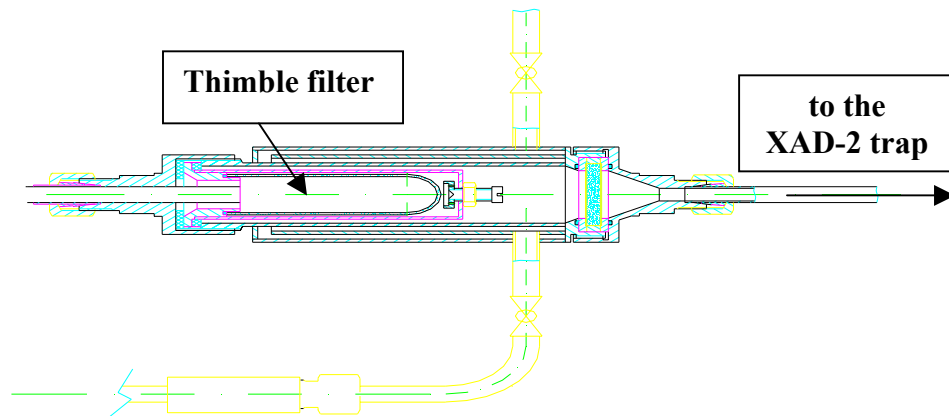


Fig. 3: Thermostatic filtration chamber

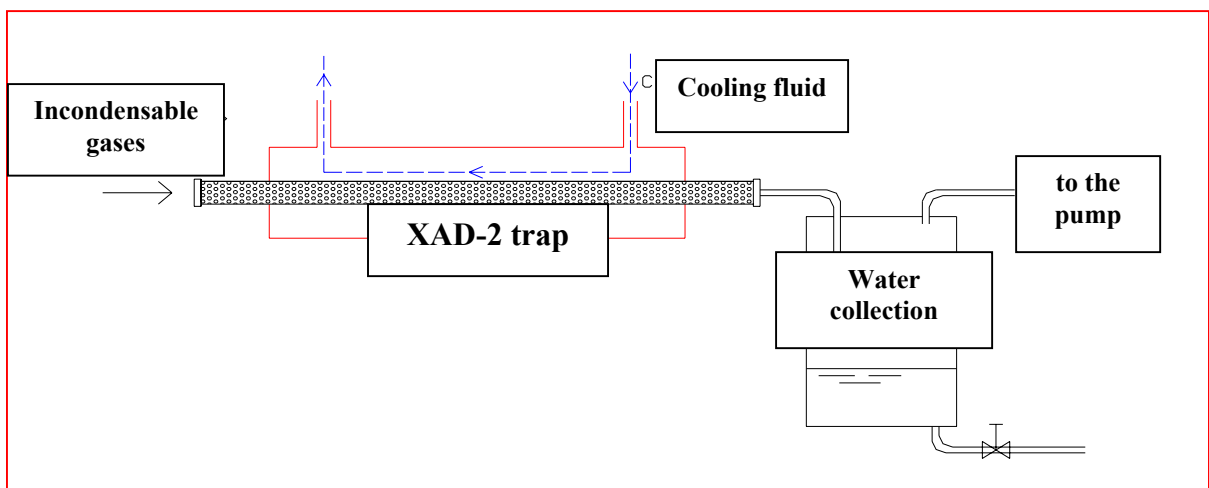


Figure 4 : Thermostatic XAD-2 Trap

The probe has been tested to check for any pressure drop in the conjunction parts. The tests have been carried out by setting up the whole sampling train and by using a sampler able to maintain the flux constant and to register the pressure drops. Tests were carried out with different sampling fluxes (in the range 2-18 L/min) and with room

temperature. The highest flux was found to be 12 L/min, as a compromise between isokineticism and a suitable particles dragging.

Sampling tests using the proposed device have been carried out in the afterburning chamber of a hospital waste incineration plant where temperatures varied in the range 910-1200 °C. Comparative tests were also carried out in the heat exchanger of the same plant, where temperatures varied in the range 190-350 °C, by using a thermostated titanium probe with the EN-1948 filter/condensation method and the proposed sampling device. In this first case, we used quartz fiber filters, followed by a condensation system and by a XAD 2 trap. In the tests 1-3 and 5-6-7 hospital wastes were burned, in the tests 4 and 8 cemeteries waste, mainly consisting of coffins with accompanied materials. Tests 1-3 in the afterburning chamber were discarded for problems in isokinetic sampling due to the high presence of coarse particulate matter. For this reason along each tests up to three thimble filters were changed. In spite of temperatures higher than 1100 °C in the afterburning chamber, very high PCDD/F concentrations were found, especially for the tests with cemeteries with respect to hospital wastes. The homologue relative distribution showed a major abundance of the less chlorinated PCDF, whereas PCDDs had a more homogenous distribution (Table 2). No correlation with operating temperature was found.

Table 1: PCDD/F in the afterburning chamber (ng/Nm³)

Tests	4	5	6	7	8
T ₄ CDD	284.5	32.8	143.1	147.1	433.8
P ₅ CDD	289.2	28.3	114.6	125.8	492.9
H ₆ CDD	410.5	328.1	107.2	97.1	338.7
H ₇ CDD	375.5	362.7	64.2	92.4	124.1
O ₈ CDD	79.3	84.5	8.5	25.3	29.5
T ₄ CDF	630.7	788.1	396.7	546.4	1442.8
P ₅ CDF	379.9	641.6	375.2	391.5	1090.3
H ₆ CDF	335.3	112.2	145.0	155.2	529.7
H ₇ CDF	244.6	29.8	51.1	71.7	155.2
O ₈ CDF	57.5	6.4	10.9	17.3	20.3
PCDD/Fs	3086.8	2414.5	1416.4	1669.8	4657.3

Table 2: Relative homologue distribution in the post combustion chamber (%)

Tests	4	5	6	7	9
T ₄ CDD	9.2	1.4	10.1	8.8	9.3
P ₅ CDD	9.4	1.2	8.1	7.5	10.6
H ₆ CDD	13.3	13.6	7.6	5.8	7.3
H ₇ CDD	12.2	15.0	4.5	5.5	2.7
O ₈ CDD	2.6	3.5	0.6	1.5	0.6
T ₄ CDF	20.4	32.6	28.0	32.7	31.0
P ₅ CDF	12.3	26.6	26.5	23.4	23.4
H ₆ CDF	10.9	4.6	10.2	9.3	11.4
H ₇ CDF	7.9	1.2	3.6	4.3	3.3
O ₈ CDF	1.9	0.3	0.8	1.0	0.4
PCDDs	46.6	34.6	30.9	29.2	30.5
PCDFs	53.4	65.4	69.1	70.8	69.5

In table 3 PCDD/F concentrations after the heat exchanger by using a thermostated titanium probe are reported. It is well known that the conditions in the heat exchanger could be critical for PCDD/F De-Novo synthesis. The presence of particles on the cold surfaces of the heat exchanger seems to be the controlling factor for such event [4, 5]. The concentrations values were always lower than the corresponding values in the afterburning chamber and no increase was reported. This evidence could be explained considering that sampling inside the afterburning furnace was performed before the thermal reaction completion. PCDD/F concentrations in the heat exchanger showed a good correlation with particulate concentration and temperature (Fig. 4 and 5), and a positive correlation with residence time (Figure 6), thus confirming the literature evidences. No correlation was found with the other parameters.

The PCDF/PCDD ratio slightly increased with respect to afterburning chamber (table 4), according to literature [3]. The tests with predominance of cimiteries waste showed a marked increase of T₄CDF, the other ones a slight increase of high-chlorinated congeners as reported also by other authors [6].

Table 3: PCDD/F in the Heat exchanger (ng/Nm³)

Tests	1	2	3	4	5	6	7	8
T ₄ CDD	8.0	22.3	24.5	62.1	10.4	2.1	7.8	0.9
P ₅ CDD	75.1	15.7	47.3	6.1	19.3	3.2	8.9	2.7
H ₆ CDD	58.9	11.2	59.1	38.2	16.4	5.7	10.1	4.3
H ₇ CDD	87.4	11.1	46.0	32.6	28.6	16.4	15.1	4.2
O ₈ CDD	7.0	4.9	22.6	6.0	4.4	4.9	2.9	3.6
T ₄ CDF	228.3	167.1	210.3	394.5	124.9	18.4	51.8	34.7
P ₅ CDF	207.9	71.8	133.9	157.0	50.6	7.8	54.1	6.1
H ₆ CDF	156.9	50.9	192.7	78.4	5.7	18.0	26.8	8.4
H ₇ CDF	59.8	20.6	98.8	31.3	3.9	19.6	20.0	9.6
O ₈ CDF	4.5	1.4	11.7	4.9	6.4	9.1	3.8	2.3
PCDD/Fs	893.7	377.0	847.0	811.1	270.6	105.2	201.1	76.8

Table 4: Relative homologue distribution in the heat exchanger %

Tests	1	2	3	4	5	6	7	8
T ₄ CDD	0,9	5,9	2,9	7,7	3,9	2,0	3,9	1,2
P ₅ CDD	8,4	4,2	5,6	0,8	7,1	3,0	4,4	3,5
H ₆ CDD	6,6	3,0	7,0	4,7	6,0	5,4	5,0	5,6
H ₇ CDD	9,8	2,9	5,4	4,0	10,6	15,6	7,5	5,5
O ₈ CDD	0,8	1,3	2,7	0,7	1,6	4,6	1,4	4,6
T ₄ CDF	25,5	44,3	24,8	48,6	46,2	17,5	25,7	45,1
P ₅ CDF	23,3	19,1	15,8	19,3	18,7	7,4	26,9	7,9
H ₆ CDF	17,6	13,5	22,7	9,7	2,1	17,1	13,3	10,9
H ₇ CDF	6,7	5,5	11,7	3,9	1,5	18,6	9,9	12,5
O ₈ CDF	0,5	0,4	1,4	0,6	2,4	8,6	1,9	3,0
PCDDs	26,5	17,3	23,6	17,9	29,2	30,7	22,2	20,5
PCDFs	73,5	82,7	76,4	82,1	70,8	69,3	77,8	79,5

Figure 4: Correlation between PCDD/F and particulate matter after the heat exchanger

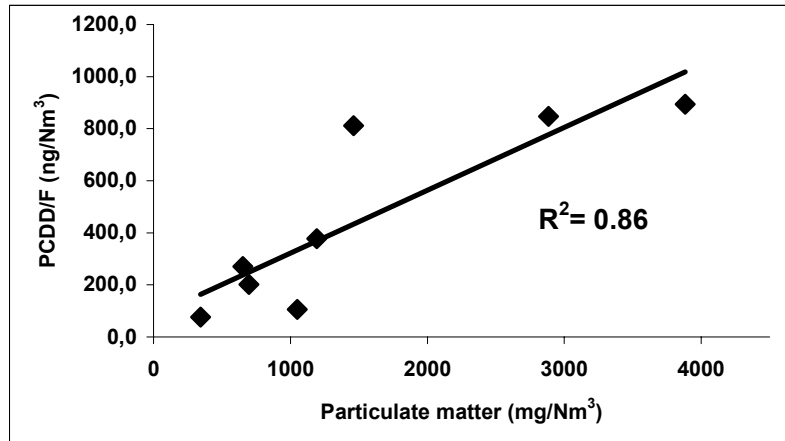


Figure 7: Correlation between PCDD/F and temperature after the heat exchanger

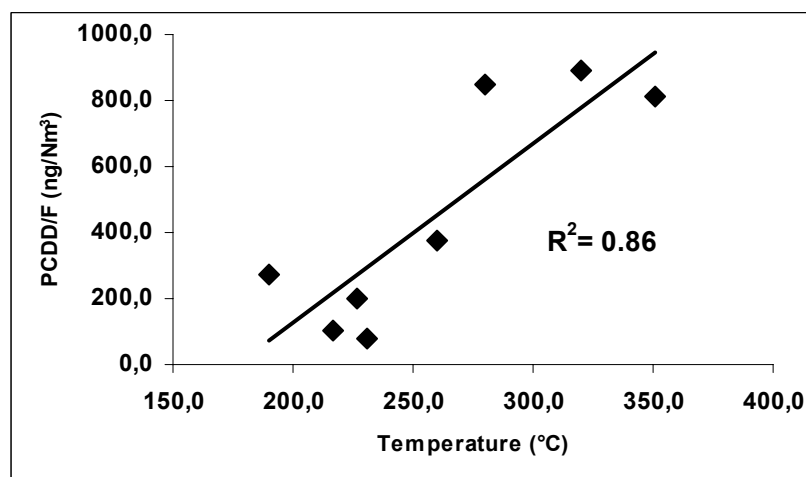
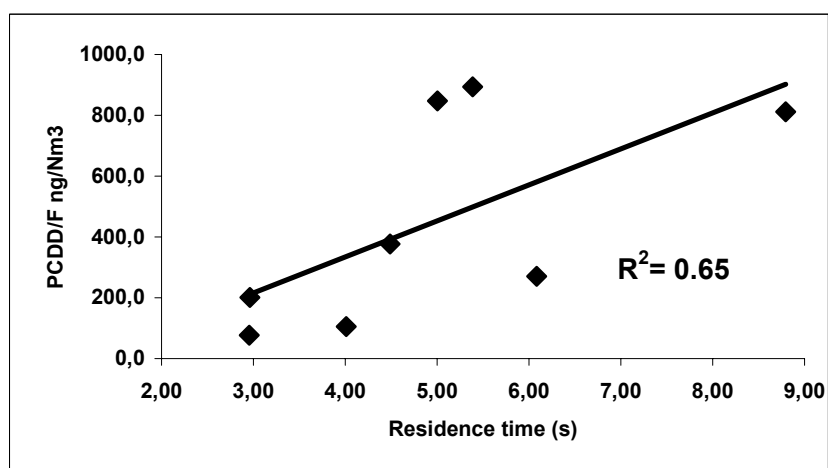


Figure 8: Correlation between PCDD/F and residence time in the heat exchanger



The tests sampled with the standard method gave lower concentration values (in the range of 10-20%) than with the proposed method. We compared therefore the different relative homologue distribution in the different sample matrices of the sampling train, for both

the sampling methods (Table 5). With the high temperature device the greatest part of congeners were found in the thimble filter and in the XAD-2 resin, whereas the concentration in the condensation water was very low. The more volatile congeners, such as T₄CDF and P₅CDF were found in the XAD-2 trap, and the heavier congeners as H₇CDD/F and O₈CDD/F were mainly found in the thimble filter. The recovery rates calculated on the sampling standards were quite good (mean 70 %) using ASE (accelerated solvent extraction) method.

As regard as the filter/condensation method the distribution of the light congeners and of the heavier ones associated with fine particles in the three different matrices is more homogenous. In this case, the fine particles pass through the first filter, then in the condensation device and finally in the adsorbing trap. The recovery rates of the heavier congeners are lower, since the liquid-liquid extraction of particles from the water matrix is less efficient and these congeners can be underestimated, thus resulting to a lower total concentration.

Table 5: Mean Relative distribution in the filtering matrices (%)

	High temperature device				EN 1948 method			
	Thimble filter	XAD	water	Total distribution	Filter	XAD	water	Total distribution
T ₄ CDD	36	55	9	4	34	24	42	4
P ₅ CDD	36	57	7	7	29	23	48	5
H ₆ CDD	45	50	5	6	45	28	27	5
H ₇ CDD	60	35	5	11	55	25	20	7
O ₈ CDD	70	24	6	6	65	24	11	2
T ₄ CDF	33	59	8	24	29	31	40	37
P ₅ CDF	41	55	6	16	27	35	38	19
H ₆ CDF	53	43	4	10	36	28	36	13
H ₇ CDF	60	35	5	11	49	25	26	7
O ₈ CDF	65	36	3	5	58	31	11	1

Conclusions

The adopted device was confirmed to be suitable for high temperature sampling in presence of high presence of halogenidric acids (as in incineration plant). The sampling device was used for the evaluation of the afterburning chamber temperature on PCDD/F appearance, but no correlation was observed. Unfortunately, the sampling was carried out before complete oxidation and the effect on DeNovo reformation could not be well evaluated. Otherwise, the heat exchanger conditions (temperature, particulate matter and residence time) were confirmed to be critical parameters for PCDD/F appearance.

The sampling device allowed to better characterise the sample, proving that the adopted sampling system can have a strong influence on congeners distribution. The use of a sampling train consisting in a first filtering system (quartz fiber filter or quartz wool basket) followed by a adsorbing resin (as XAD) is recommended.

References:

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