

MONITORING THE DESTRUCTION OF INDIVIDUAL TOXIC 2378-SUBSTITUTED PCDD/F IN SOLID MATRICES BY HYDROTHERMAL OXIDATION USING GC-MS/MS QqQ

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Introduction

The environmental release of chlorinated dioxins and furans (PCDD/F) has been a major concern to researchers, scientists and policy makers for a long time now. Mitigation of PCDD/F release into the environment has been attempted by a variety of techniques including activated carbon capture, in-situ destruction of formed PCDD/Fs and suppression of PCDD/F formation. The presence of PCDD/Fs in incineration flyash and other solid matrices like sewage sludge render make the disposal of these samples very expensive. Moreover, the disposal of PCDD/F-laden activated carbon traps may pose significant problems in the future, as the number of incineration plants increase.

Oxidation of organic compounds in subcritical and supercritical water has been investigated by several researchers¹⁻³. The process involves the solubilization of hitherto non-water soluble organic substances by high-temperature high-pressure water, creating a mono-phasic medium where the oxidation rates become high. The hydrothermal medium itself provides a distinct set of properties that can be advantageous to all organic sample types. In the hydrothermal oxidation process, organic carbon and hydrogen atoms are converted to innocuous carbon dioxide and water, respectively. Atoms such as chlorine can be released as diluted hydrochloric acid or may combine with metals to form the corresponding metal chloride salts.

In this work, the oxidation of toxic 2378-substituted PCDD/Fs using 30 wt% hydrogen peroxide solution as the oxidant. The extent of destruction/removal of each individual PCDD/Fs was monitored using GC-MS/MS QqQ fitted with a low-temperature CP-Sil 88 column. This column has been found to be very reliable for the specific analysis of all the seventeen 2378-substituted PCDD/Fs⁴. Although, the decomposition of POPs in solid matrices using supercritical water, the results were often presented in terms of bulk properties such as TOC reduction or CO₂ production. In this work, the destruction of individual PCDD/F has been monitored in order to understand the reactions of each congener.

Materials and methods

Certified reference flyash (BCR-490) samples was obtained from the European Commission JRC-IRMM and used as received. Hydrogen peroxide was obtained from Sigma-Aldrich, UK. The details of the batch reactor used in this work have been provided in an earlier paper⁵. Briefly, the reactor consists of a 75 ml Inconel vessel and it rated to a temperature of 600 °C. The maximum working pressure is 51MPa. It is fitted with a pressure gauge and a thermowell housing a thermocouple for reading the internal pressure and temperatures, respectively.

In each hydrothermal oxidation experiment, 2.0 g of flyash was weighed into the reactor. Between 0.0 and 7.5 ml of the 30wt% hydrogen peroxide was added and the total liquid volume made up to 20 ml by adding deionized water. The total liquid volume of 20 ml had been determined to give the pressures required for the reactions⁵. The reactor was then sealed, placed in a heater and heated to the desired reaction temperature at a heating rate of 12 °C/min. On reaching the desired reaction conditions, the reactor was quickly withdrawn from the heater and rapidly cooled to quench the reaction. The results are presented in terms of changes in the concentration profiles of individual PCDD/F during the oxidation process.

Analysis of PCDD/Fs

The isomeric analysis of the seventeen PCDD/Fs with chlorination at their 2378-positions was carried out with a Varian 430-GC with a 320-MS triple quadrupole analyzers (GC-MS/MS QqQ). The GC separation of PCDD/F

was carried out using a Varian CP-Sil 88 capillary column for dioxins (50 m × 0.25 mm I.D., 0.25 μm film thickness). Helium was used as a carrier gas at a constant flow-rate of 1 ml min⁻¹. 2 μl samples were injected to the GC in splitless injection mode at 270 °C. The column oven temperature program was initially 140 °C held for 2 min., ramped at 45 °C min⁻¹ to 190 °C with no holding time, and ramped at 5 °C min⁻¹ to 240 °C held for 31.89 min. giving the total runtime of 45 min. This method enabled the rapid elution of the solvent in injected sample matrices and best separation of PCDD/F throughout the column. The transfer line temperature was held at 250 °C and once the PCDD/Fs arrived at the ion volume, which was maintained at 200 °C, ionization was by EI (electron impact ionization). The detector was set to operate using the Extended Dynamic Range (EDR) with centroid scan position. Details of the MS conditions are shown in Table 1.

Table 1: MS conditions used in this work

MS Conditions	
Tune	EI Autotune
Filament Current	50 μA
Electron Energy	70 eV
Source Temperature	200 °C
Source Pressure	18 mTorr
CID Gas Pressure	1.50 mTorr
Manifold Pressure	7.7 μTorr

The extraction of samples and preparation of extracts for GC analysis was based on USEPA Method 1613⁶.

Results and discussion

Figure 1 presents the results of the analysis of the reference materials using the analytical procedure developed⁴. These results have been compared to the certified values and are within acceptable limits in terms of the coefficients of variation.

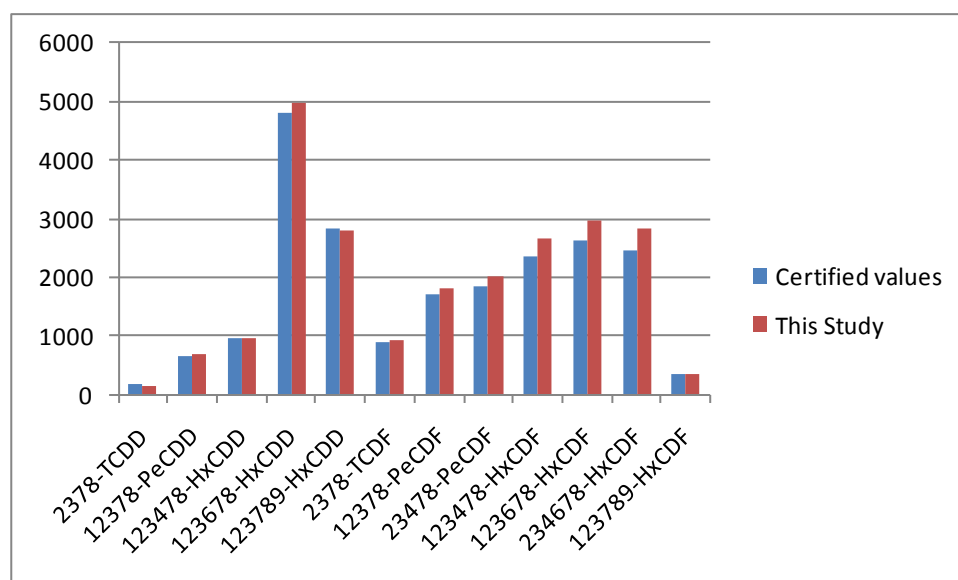


Figure 1: Results of the analysis of BCR-490 reference flyash

Table 2 shows the changes concentration profiles of each of the seventeen 2378-substituted PCDD/Fs with respect to oxidant loading at 400 °C and 26MPa. The effect of the oxidant on the destruction of some of the pollutants can be seen clearly from the data. Without oxidant, some congeners showed appreciable reduction by the action of supercritical water alone. Congeners such as 12378-PeCDF reached up to 73% reduction the oxidant , whereas the most toxic 2378-TCDD only decomposed by about 1%. However, with increasing oxidant concentration, the decomposition rate of all the congeners increased considerably. At an oxidant ratio of 0.25, all the PCDD/Fs were individually destroyed by more than 70 %; and at the oxidant ratio of 0.375, more than 82% destruction was observed. Although, the percentage reduction in each congener was high, it appeared that the reaction condition at 400 °C and 26 MPa was not sufficient to completely destroy the PCDD/Fs.

Table 2: Percentage reduction in PCDD/F concentrations after oxidation at 400 °C, 26MPa in relation to oxidant concentration

Volume ratio of oxidant	% Congener Reduction					
	0	0.025	0.075	0.125	0.25	0.375
PCDD/F						
2,3,7,8 TCDD	1.04	7.43	32.6	77.0	84.1	87.6
2,3,7,8 TCDF	50.8	51.9	69.9	71.2	76.2	84.7
2,3,4,7,8 PeCDF	44.5	66.8	84.0	83.0	83.6	83.4
1,2,3,7,8 PeCDD	39.3	69.1	71.4	87.9	91.7	93.4
1,2,3,4,7,8 HxCDF	43.9	43.8	95.5	96.5	94.5	95.6
1,2,3,6,7,8 HxCDF	44.4	74.9	92.1	96.8	96.8	98.5
1,2,3,7,8 PeCDF	73.6	78.3	91.6	94.8	97.0	97.3
1,2,3,4,7,8 HxCDD	4.90	22.3	67.8	80.9	95.6	95.1
1,2,3,6,7,8 HxCDD	5.19	9.3	51.1	75.9	82.5	82.0
1,2,3,7,8,9 HxCDD	24.6	49.9	62.9	66.1	70.5	83.9
1,2,3,4,6,7,8 HpCDF	53.9	61.6	75.6	79.6	87.7	92.6
1,2,3,7,8,9 HxCDF	14.0	61.7	77.4	93.4	95.5	98.4
2,3,4,6,7,8 HxCDF	20.2	46.0	59.9	64.9	79.4	87.9
1,2,3,4,6,7,8 HpCDD	64.5	73.3	73.5	81.0	83.6	90.3
1,2,3,4,7,8,9 HpCDF	55.8	83.9	96.0	98.3	98.1	100
OCDF	1.43	26.7	38.5	31.0	42.1	61.6
OCDD	26.2	66.8	68.0	77.1	97.0	96.9

Subsequent oxidation experiments were carried out at 450 °C with a corresponding pressure of 34.5MPa. The results are presented in Table 3. Almost in all cases, higher destruction rates of PCDD/Fs were observed at 450 °C, compared to 400 °C, even in the absence of oxidant. It can be argued that more stringent hydrothermal reaction conditions are required for extensive removal of dioxins and furans from flyash samples. Almost 13% reduction was observed for 2378-TCDD at 450 °C compared to 1% at 400 °C. Furthermore, in general over 90% reduction was found with respect to all the seventeen congeners at 450 °C, suggesting the complete destruction of PCDD/Fs in flyash could be possible at higher temperatures or by using extended reaction times. These results are in agreement with the work of

Results also suggest that the destruction rates of PCDD/Fs may not be concentration dependent. However, the disappearance of the highly chlorinated congeners may not be due to direct mineralization but may involve dechlorination to congeners with lower degrees of chlorination. For instance, the much higher destruction rates

of 23478-PeCDD, 12378-PeCDD, 1123478-HpCDF, 1234678-HpCDD and 1234789-HpCDF may be responsible for the much lower destruction rates for 2378-TCDD observed in the absence of oxidant and at very low oxidant ratios.

Table 3:
Percentage reduction in individual PCDD/F concentrations at 450 °C, 34.5MPa in relation to oxidant concentration

Volume ratio of oxidant	% Congener Reduction					
	0	0.025	0.075	0.125	0.25	0.375
PCDD/F name						
2,3,7,8 TCDD	13.3	35.4	73.2	87.3	87.8	93.7
2,3,7,8 TCDF	52.1	59.8	72.9	76.8	87.0	91.2
2,3,4,7,8 PeCDF	60.7	67.2	86.7	88.0	89.9	92.2
1,2,3,7,8 PeCDD	65.9	86.2	90.4	91.7	92.8	94.3
1,2,3,4,7,8 HxCDF	25.6	69.7	97.3	98.0	99.0	99.4
1,2,3,6,7,8 HxCDF	58.8	80.8	97.9	99.0	99.1	99.2
1,2,3,7,8 PeCDF	33.1	77.1	93.5	97.6	97.4	97.6
1,2,3,4,7,8 HxCDD	18.1	81.3	87.7	97.3	98.0	98.6
1,2,3,6,7,8 HxCDD	21.3	57.1	79.5	88.1	89.2	90.8
1,2,3,7,8,9 HxCDD	17.4	53.1	64.8	79.4	88.7	92.4
1,2,3,4,6,7,8 HpCDF	64.4	66.9	78.5	84.9	89.8	94.6
1,2,3,7,8,9 HxCDF	19.2	79.0	91.8	94.5	98.5	99.3
2,3,4,6,7,8 HxCDF	42.2	48.0	65.1	67.8	85.8	93.9
1,2,3,4,6,7,8 HpCDD	69.2	81.0	88.5	93.7	94.3	96.1
1,2,3,4,7,8,9 HpCDF	64.1	90.9	97.4	99.3	99.8	100
OCDF	20.8	32.6	66.0	82.6	93.2	95.8
OCDD	43.5	72.0	90.3	94.3	93.9	96.2

Thus, considering that PCDD/Fs are virtually unreactive and persistent, their destruction/decomposition by the application of moderately low temperature hydrothermal oxidation may provide a cheaper and cleaner means of disposal. The changes in the TEQ values of the PCDD/Fs as a result of hydrothermal oxidation would be further evaluated.

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References:

1. Krajnc M, Levec J. (1994). *Applied Catal. B: Environ.* 3, 101-107.
2. Lin KS, Wang HP, Li MC. (1998), *Chemosphere*, 36(9), 2075-83
3. Sato T, Sugeta T, Otake K, Sato M, Tsugumi M, Hiaki T, Hongo M. (1997); *J. Chem. Eng. Jpn.* 30(4), 744-47
4. Hajizadeh Y, Onwudili, JA, Williams PT. (2011); *Waste Mgt.* .31(6)1194-1201
5. Onwudili JA, Williams PT. (2010); *Green Chemistry*, 12, 2214-222
6. USEPA, Method 1613, (1994); Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B. Washington, DC, USA