QUANTIFICATION OF DIOXINS AND FURANS IN WASTE GAS THERMAL OXIDATION PLANT EMISSIONS

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Abstract

Dioxin a stable, nonvolatile, lipophilic and poorly biodegradable chemical is produced by human as contaminant in herbicides manufacturing, waste incineration and many other industrial processes. Though the impact of dioxins on human health and animal is well known and waste incinerators are considered to be a potential source for dioxin emissions, this work has been carried out to identify and quantify these chemicals from the emissions of a waste gas thermal oxidation plant. Among three samples collected at various time period, 2,3,7,8-Tetrachloro dibenzo-p-dioxin has been quantified at trace levels along with few furan congeners.

Introduction

Persistent organic pollutants, also called POPs, are among the most dangerous chemicals ever created by humans. POPs include many pesticides, industrial chemicals and chemical byproducts such as Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin like polychlorinated biphenyls (DL-PCBs). Even at extremely low levels, dioxins are very persistent, semi volatile and mobile, traveling great distances in air and water. They are fat-soluble, bioaccumulating in humans, wildlife and fish, and are transferred from mother to fetus, in utero and through breast milk. Dioxins cause cancer, affect the immune system, thyroid, liver and kidney functions and are linked with diabetes. The main source of dioxins at present is waste incineration[1-9], with most being generated in combustion processes and released to the ambient air without being fully captured by waste-gas treatment equipment. Though the behaviour of dioxins in the environment is not fully understood, this study investigated levels of congeners of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the emissions of waste gas thermal oxidizer plant in India where the gaseous waste from the refrigerant gas manufacturing industry is being destructed thermally.

Materials and Methods

Emission samples (60-90ft^3 dry gas) were isokinetically collected over XAD-2 cartridge from the flue gas stream of a waste gas thermal oxidation system in India destructing gaseous waste comes out of refrigerant gas production. Samples were withdrawn from the gas stream and collected in the sample probe, on a glass fiber filter and on a packed column of adsorbent material (XAD-2). The samples were brought to the laboratory and soxhlet extracted with 300ml toluene for 16 hours and the extracts have been concentrated using Kuderna-Danish concentrator to a volume of 1ml. The concentrates were taken for clean up to remove interferences using multilayered silica column packed with 1g silica, 2g sodium hydroxide impregnated silica, 1g silica, 4g sulphuric acid modified silica and 2g silica, followed by alumina and carbon columns. The final elute was concentrated to a volume of 1ml and taken for GC-MS analysis[10]. PCDD/Fs were determined by a HRGC-MS operating in electron ionisation mode (EI) and selected ion monitoring (SIM) and scan modes (KONIK Q12 Series) equipped with a SP-2331 column (Supelco, USA) fused silica capillary column (60m, 0.25mm ID, 0.25µm layer thickness), and split less injection. The gas chromatograph temperature was programmed as follows: 90°C, held for 1 min, increased by 8°C/min to 300°C, held for 20 min, high purity Helium was used as the carrier gas. Initial calibrations and column performance checking were carried out using standards of dioxin and furan mix obtained from AccuStandard, New Haven, USA.

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Results and Discussion

From the results obtained by analyzing three samples collected at different period shows that polychlorinated dibenzofurans (PCDFs) are predominant in the stack flue gases of waste gas thermal oxidizer plant. The analytical results of first sample shows the absence of dioxin congeners and dominance of furan congeners whereas second and third sample showed the presence of 2,3,7,8-Tetrachloro dibenzo-p-dioxin in considerable level along with the PCDF congeners.

Table.1 DIOXINS AND FURANS IN FLUE GAS COLLECTED FROM A WASTE GAS THERMAL OXIDISER PLANT IN INDIA (All values are given in µg/Nm^3)

PCDD/F Congeners	SAMPLE 1	SAMPLE 2	SAMPLE 3
2,3,7,8-TCDD	ND	0.0075	0.015
1,2,3,7,8-PeCDD	0.005	ND	0.006
1,2,3,4,7,8-HxCDD	ND	ND	ND
1,2,3,6,7,8-HxCDD	ND	ND	ND
1,2,3,7,8,9-HxCDD	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	ND	ND	ND
1,2,3,4,6,7,8,9-OCDD	ND	ND	0.002
2,3,7,8-TCDF	0.0052	0.0034	0.0025
1,2,3,7,8-PeCDF	0.0018	0.0012	0.0016
2,3,4,7,8-PeCDF	0.015	0.015	0.00085
1,2,3,4,7,8-HxCDF	0.0019	0.0019	0.00026
1,2,3,6,7,8-HxCDF	0.0020	0.0017	0.00026
2,3,4,6,7,8-HxCDF	ND	ND	ND
1,2,3,7,8,9-HxCDF	0.0015	0.0013	0.00025
1,2,3,4,6,7,8-HpCDF	ND	0.00054	0.00082
1,2,3,4,7,8,9-HpCDF	ND	ND	ND
1,2,3,4,6,7,8,9-OCDF	12.023	ND	ND

The congener profiles of the 2,3,7,8-substituted PCDD/Fs are selected as signatures of the emission of waste gas thermal oxidizer plant. Table 1 shows the congener profiles of the 17 PCDD/Fs detected from the stack flue gas samples. It has been observed that level of pentachloro dibenzofuran was high in sample 1 whereas octachloro dibenzofuran dominates along with the presence of highly toxic 2,3,7,8-TCDD in samples 2 and 3. Chromatograms obtained were compared with the NIST mass library and correlated with the intensities of the peak obtained for dioxin standard mix. The congener profiles of the thermal oxidizer plant emissions are similar to those presented in other research with reference to the literature review[11-12]. Overall observations show that PCDFs are dominant in the stack flue gas. The most abundant congeners of are 2,3,4,7,8-PeCDF, 2,3,7,8-TeCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF (in order of quantity). The presence and quantity of dioxin and furan congeners are influenced by the waste gas quantity and the operating conditions of the thermal oxidizer plant. It has been confirmed that the emissions of waste gas thermal oxidation plant contains dioxin and furan congeners at ultra trace levels but the presence of 2,3,7,8-TCDD in some samples gives a warning signal to the thermal oxidizer performance. Since the dioxin problem across the globe and in India as well is very sensitive, the name of the plant and its location is not disclosed here.

Acknowledgement

We thank Director General, Council of Scientific and Industrial Research, New Delhi and Director, National Institute for Interdisciplinary Science & Technology, Thiruvananthapuram for the financial assistance and constant support.

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