POLYHALOGENATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN THE EXHAUST FUMES AND FLY ASHES OF MUNICIPAL WASTE AND INDUSTRIAL INCINERATORS

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Abstract

Screening of four municipal waste incinerators (MSWI) and one industrial incinerator were investigated by High Resolution Gas Chromatography – High Resolution Mass Spectrometry (HRGC-HRMS) for polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) and mixed polychlorinated-brominated dibenzo-*p*-dibenzodioxins/furans (PBCDD/Fs). For the purpose of these investigations the complete dioxin-balance output from fly ashes and the exhaust fumes of MSWI was done. In the exhaust fumes very low PBDD/Fs concentrations were detected. The fly ashes contain slightly amount of PBDD/Fs. In both of them, we are found huge amounts of PXDD/Fs but with fewer amounts of highly brominated molecules in the case of exhaust fumes. The fly ashes contain higher PCDD/F-concentrations of up to 45000 ng I-TEQ/g, PBDD/F-concentrations of up to 0.1 ng/g and PBCDD/F-concentrations of up to 81.8 ng/g.

Introduction

From the literature [1] it is known, that fly ash and exhaust of MSWI contain few hundred ng I-TEQ/g or /Nm^3 PCDDs and PCDFs. Furthermore investigations [2] show that halogenated dioxins and furans are formed from organo-carbon and organohalogen at higher temperatures (de novo synthesis) [3] with help of supported catalist like metal chloride. These organohalogen compounds were provided by the incineration of different manufactured materials such as PVC or electronic board etc… For the purpose of these investigations the complete dioxin-balance output from the fly ashes and exhaust of MSWI was done. Incineration of chlorinated compound and brominated compounds (such as flame retardants) are well known to generate highly toxic compounds like polyhalogenated dioxins and furans (PXDD/Fs). The following analysis of output of 5 different MSWIs were done for PCDD/Fs, PBDD/Fs and PBCDD/Fs.

Experimental

Incinerator

MSWIs use fluid bed oven and different process to make the clean up of the exhaust fumes (ash filters or electro-filters and wet clean up).

Sampling

The emission sampling was carried out using an Environmental probe from Environment SA (figure 1).

The sampling of the exhaust gas followed the European Norm (EN1948-1)[4] in isokinetic conditions.

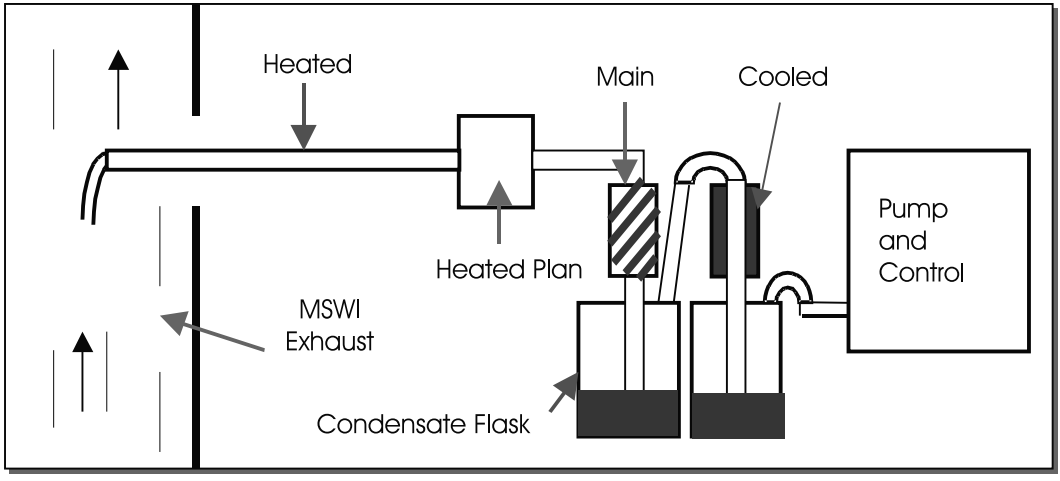

Figure 1. Glass apparatus CAE express for sampling of PXDD/F in exhaust fumes (X=CL or Br)

The efficiency of the sampling was examined by addition of the three labelled compounds: $^{13}C_{12}$-1,2,3,7,8-PeCDF, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF & $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF.

Chemicals

The native and labelled (^{13}C) compound of dioxins and furans studied were provided from Wellington laboratories (Ontario, Canada). These standard solutions were transferred to a CERTAN capillary ampoule and stored at 20 °C. All the solvents were Pesticide or HPLC grade and purchased from SDS. One exception concerns n-nonane which was provided by Accros Organics.

Extraction

Previously we have extracted in sub-critical fluid condition with commercial apparatus purchased from Dionex. For these extractions, a 0.5g aliquot of a composite of fly ash was taken and mixed with 10g of Celite 545 and were transferred in an extraction cell for ASE 200.

Clean up

The clean up was made by using the method described elsewhere[5].

Quantification

The quantification was realised with the method of isotopic dilution for the PCDD/Fs. We fortified the sample with 13 labelled PCDD/Fs, only these were used to quantify. Before injection into the gas chromatograph the surrogate standard $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD was added to the sample and then used as internal standards to calculate recoveries.

In suspicion of formation of PBDD/F and PBCDD/F the following labelled brominated and brominated/chlorinated compounds are added: $^{13}C_{12}$-2,3,7,8-TBDD and $^{13}C_{12}$-1Br-2,3,7,8-PeCDD.

HR-GC/HR-MS analysis

The hyphenated technique such as high resolution gas chromatograph-high resolution mass spectrometer represent the appropriate tool to obtain accurate results for the analysis of PCDD/Fs,

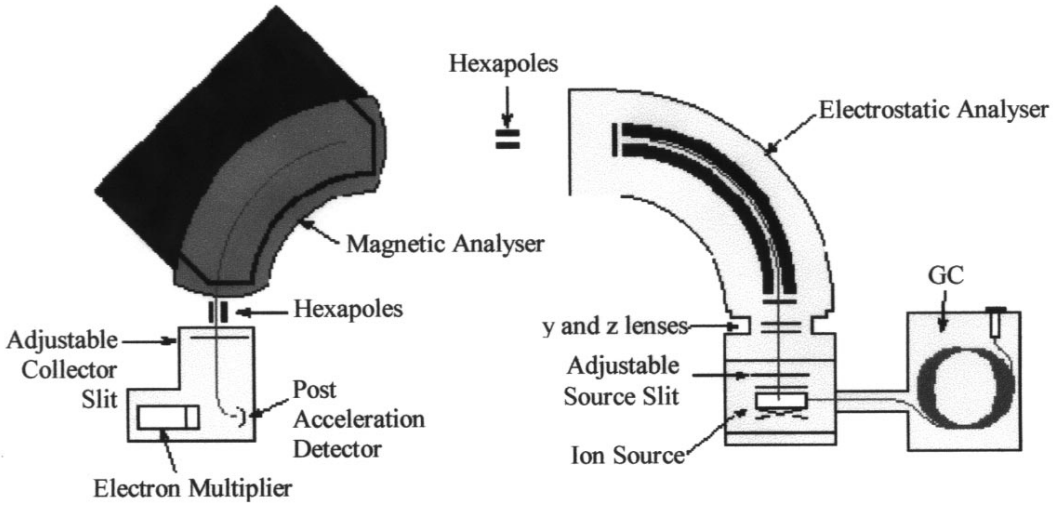

Figure 2. HR-MS Autoconcept scheme

PBDD/Fs and PBCDD/Fs. The GC are provided by Agilent and the mass spectrometer come from MSI (Manchester) (figure 2).

An Autoconcept mass spectrometer from Mass Spectrometry International (Manchester) with geometry EB was used (presented in figure 2). The quantification limits range from 10 to 50 fg/ml injected and the linearity is in the order of 10^8. Analysis of PCDD/F was conducting in EI mode by monitoring the M^+, $(M+2)^+$, or the most intensive ions of the isotope cluster. In every multi-ion detection cycle, two fragments of the reference compound PFK were used as look mass and check mass

The mass spectrometer was connected to a GC 6890 from Agilent (USA) equipped with GC PAL autosampler from CTC Analytics (Switzerland). Chromatographic separation was performed on a 60 m x 0.25 mm I.D. DB5-MS 5 % diphenyl/95 % dimethylsiloxane capillary column from J&W with a 0.1 mm film thickness. The initial column temperature was set at 140 °C for 1 min, then increased to 210 °C (10 °C/min, 1 min hold), programmed to 315 °C (3 °C/min, 10 min hold),. The injector was operated in splitless mode at 305°C. The transfer line was at 300 °C too. The flow rate of Helium (6.0 grade from Linde) carrier gas was 1 ml min^{-1}.

Results

In the exhaust fumes of the incinerators, the PCDD/F-concentrations were in the range of 0.052 and 4.7 ng I-TEQ/Nm^3.

These results show, that the PCDD/F-emissions of all incinerator were not obviously below the European limit which 0.1 ng I-TEQ/Nm^3 and it could be correlated with the exhaust clean up technique. This means, that in relation to the PCDD/F-emissions further actions have to be studied to obtain a significant decrease of this PCDD/Fs level.

Besides the PCDD/Fs investigation analysis for PBDD/Fs and PBCDD/Fs were done (figure 3).

The data about these compounds were not listed. In exhaust gas and fly ashes there are only very small amount of PBDD/Fs. For the mixed PBCDD/Fs the concentrations are relatively high compared to the pure brominated compounds and were in the wide range of 0.1 to 81.8 ng/g for fly ashes and 0.1

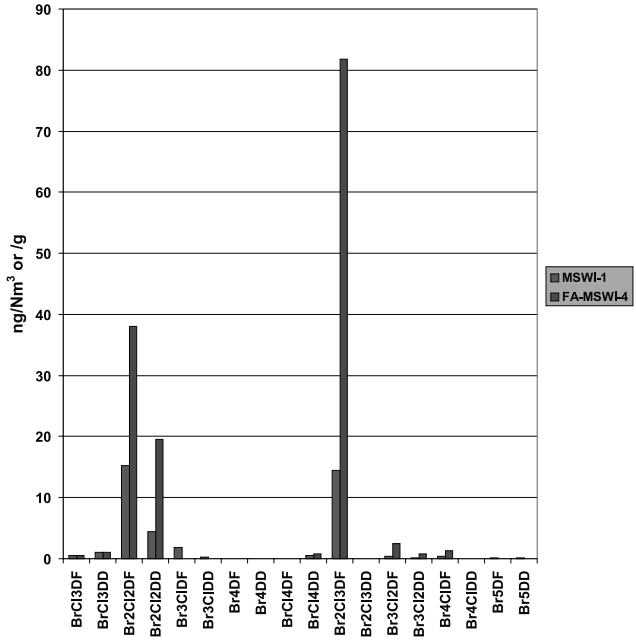

Figure 3. PBDD/F & PBCDD/F-concentrations in MSWI exhaust fumes and Fly Ashes from MSWI

to 15.3 ng/Nm^3. We could noted one discrimination concerning the most heavy molecules (high brominated rate) between fly ashes and gas samples (with low level of high brominated compounds). These high concentrations for the mixed PBCDD/Fs and the numerous of isomers in regards of the formation energy must be considerate as an argument for the De Novo synthesis of these compounds.

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