

NOVEL TOOL FOR PEAK RECOGNITION AND QUANTIFICATION OF MIXED HALOGENATED DIBENZO-*P*-DIOXINS AND FURANS (X=CL,BR) : SYNTHESIS OF PXDD/FS AND RELATED THEORETICAL CALCULATIONS

Hugues Preud'homme^{1,2}, Martine Potin-Gautier¹

¹Laboratoire de chimie Analytique (LCABIE-UMR5034) Université de Pau et des Pays de l'Adour
64013 Pau cedex France. e-mail : hugues.preudhomme@univ-pau.fr

²Laboratoires Départementaux des Pyrénées Atlantiques rue des Ecoles 64150 Lagor FRANCE

Abstract

Up to date there are no guidelines governing the toxicological importance of mixed halogenated dibenzodioxins and furans (PXDD/Fs) due to the absence of analytical methods for isomer specific analysis and consequent calculations of their associated toxicities. A second reason could be the existence of numerous isomers for these compounds and the absence of standards. Synthesis of some specific isomers of PXDD/Fs with the help of theoretical calculations could be useful in their identifications and specific analysis.

The reaction (isomerisation and condensation) of halogenated phenol gives specific polyhalogenated dibenzofurans and dioxins. The identification of the reaction products by an hyphenated technique (High Resolution Gas Chromatography – High Resolution Mass Spectrometry) and some theoretical consideration (with help of Hyperchem 6.0) gives us a specific identification of some polyhalogenated dioxins and furans isomers. A mixture of these specific compounds can be used as a “windows defining mixture”. The theoretical chemistry of these compounds has been investigated and a qualitative-quantitative relationship with PCDD/Fs established. The values of the relative response factor and the elution order can be predicted for a DB5-MS column and a linear temperature program. It is very helpful to identify the peak positions of any polyhalogenated isomers as standards are not available.

Introduction

From the literature [1] it is known, that fly ash and exhaust of MSWI contain few hundred ng I-TEQ/g or /Nm³ 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 catalyst 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

ANALYSIS I

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).

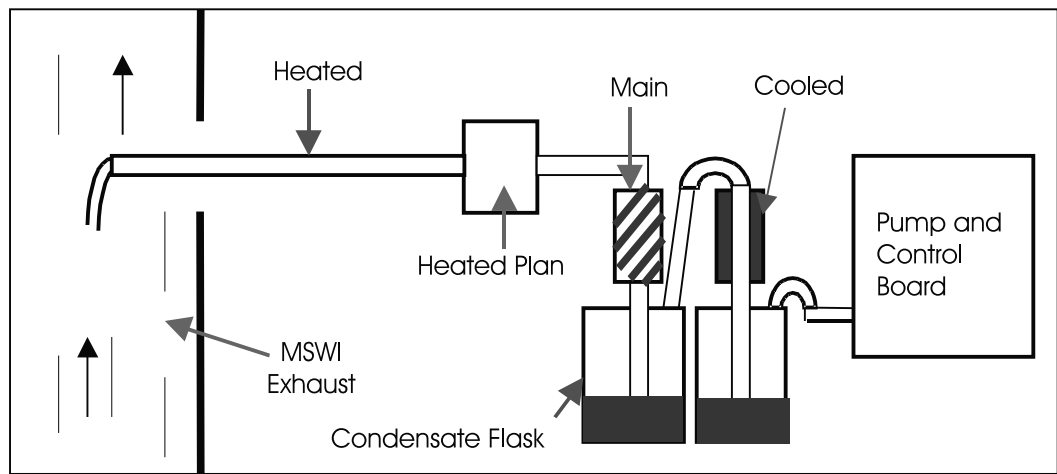


Figure 1. Glass apparatus CAE express for sampling of PXDD/F in exhaust fumes (X=CL or Br)

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

The efficiency of the sampling was examined by addition of the three labelled compounds: $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF & $^{13}\text{C}_{12}$ -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 $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -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: $^{13}\text{C}_{12}$ -2,3,7,8-TBDD and $^{13}\text{C}_{12}$ -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, PBDD/Fs and PBCDD/Fs. The GC are provided by Agilent and the mass spectrometer come from MSI (Manchester) (figure 2).

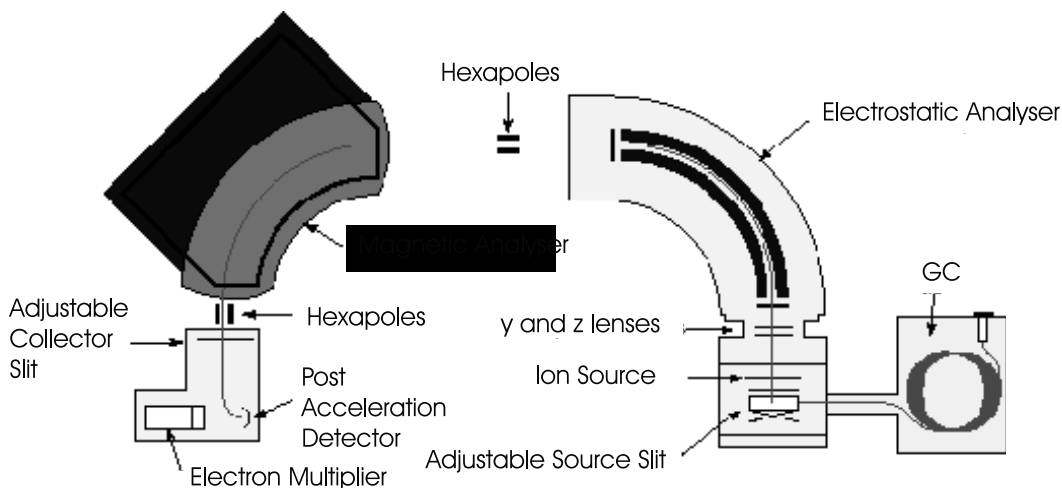


Figure 2. HR-MS Autoconcept scheme

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/Nm³.

These results show, that the PCDD/F-emissions of all incinerator were not obviously below the European limit which 0.1 ng I-TEQ/Nm³ 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

ANALYSIS I

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 to 15.3 ng/Nm³. 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.

The theoretical calculations and synthesis of specific mixed halogenated dioxins and furans could give us a beginning of response concerning isomers identification and quantification.

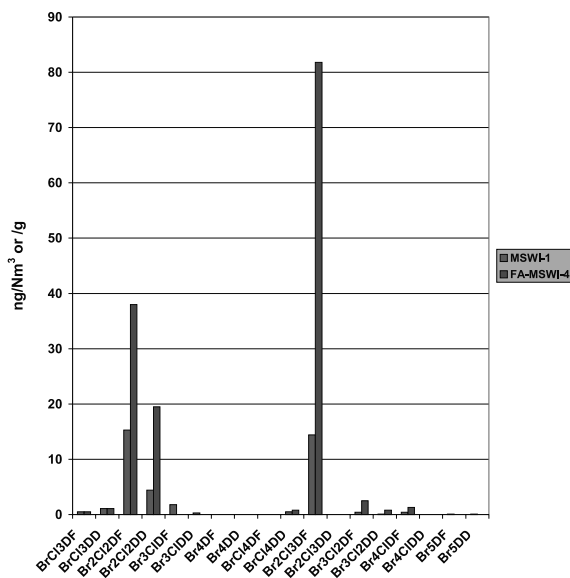


Figure 3. PBDD/F & PBCDD/F-concentrations in MSWI exhaust fumes and Fly Ashes from MSWI

Acknowledgements

The authors would like to thank EPLD and ANRT for the material financial helps, Pr Kettrup, Karl Werner Schramm (GSF-Munchen), Bernhard Henkelmann (GSF-Munchen) for advices, Malcolm Kimber (MSI) and Jacek Tronczynski for stimulating discussions.

References

1. Horstmann, M., Mc Lachan, M., *Organohalogen Compounds*, 1995, 22, 309
2. Hutzinger, O., Fiedler, H., *VDI-Berichte*, 1987, 634, 17
3. Vogg, H., *Organohalogen Compounds*, 1995, 22, 31
4. European Community, *AFNOR*, EN1948-1, 1997
5. Wu, W.Z., Schramm, K.W., Henkelmann, B., Xu, Y., Yediler, A., Kettrup, A., *Chemosphere*, 1997, 34, 191