Correlation between PCDD/F, PCB and PClBz in coal / waste combustion. Influence of various inhibitors

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Introduction

In the flue gas of co-combustion of solid waste and coal in a laboratory scale furnace high concentrations of PCDD/F, PCB and PClBz have been detected. These toxic emissions have been reduced by the help of various inhibitors added to fuel before incineration. Some of the inhibitors, suppress the PCDD/F, PCB and PClBz emission by more than 98-99%. It was found also that with decreasing the percentage of inhibitor the effect is correspondently reduced.

Knowledge of the congener pattern and homologue profiles of PCDD/F, PCB and PClBz is important to elaborate the mechanism of formation and inhibition of the toxic compounds formed during co-combustion of solid waste and coal. Statistical analysis such as Principle Component Analysis (PCA) and Correspondence Analysis (CA) are used to separate the samples according their toxicity and to detect easily the best correlated patterns.

Chlorinated benzenes are known as surrogates for the emissions of PCDD and PCDF [1,2]. In this study we focused on the relationship between dioxins and other chlorinated compounds. These investigations are done separately for the samples with higher and lower toxicity.

Matrials and Methods

Laboratory scale experiments: The fuel-types used in this study are lignite coal from Puertollano (Spain), pre-treated municipal solid waste (Rethmann Plano GmbH) and used PVC (waste from ground carpet). The weight percentage content for the lignite coal is 80% of the total fuel. The chlorinated compounds are 20% with a 13.3 : 6.7 ratio of the solid waste to PVC. In the inhibitor experiments, the inhibitor is added as 5, 3 and 1 % of the fuel. The remaining percentage fuel is mixed in the same manner mentioned above for samples without additives. Three different inorganic N- and S-compounds are investigated as inhibitors. A laboratory scale horizontal split-tube furnace (Carbolite, England) is used for the experiments. The combustion experiments are performed according to the same procedure each time in order to achieve comparable results.

The identification and quantification of tetra- to octachloro- isomers of PCDD/F is executed on a HRGC/HRMS [3]. The analysis of PCB and PClBz is done by GC/MS where the mono – deca chlorinated PCB isomers and tetra-hexa chlorinated PClBz are separated gas chromatographically

by 5%-Phenylphase-column and coupled with mass spectroscopy. All resulting values are presented in pg/sample combusted material.

Database: The total number of samples is 21 including samples treated without and with inhibitor and different percentage of inhibitors. The matrix used for statistical investigation of PCB, PClBz and PCDD/F include 36 variables, see Tab.1.

V1	TCDD	V13	PCDD/F *	V25	HxCDF *
V2	PeCDD	V14	TCB *	V26	HpCDF *
V3	HxCDD	V15	PeCB *	V27	TCDD/F *
V4	HpCDD	V16	HxCB *	V28	PCDD/F *
V5	OCDD	V17	HpCB *	V29	HxCDD/F *
V6	Sum PCDD	V18	PCB *	V30	HpCDD/F *
V7	TCDF	V19	TCDD *	V31	1,2,3,5-TClBz
V8	PeCDF	V20	PeCDD *	V32	1,2,4,5-TClBz
V9	HxCDF	V21	HxCDD *	V33	1,2,3,4-TClBz
V10	HpCDF	V22	HpCDD *	V34	PeClBz
V11	OCDF	V23	TCDF *	V35	HxClBz
V12	Sum PCDF	V24	PeCDF *	V36	Sum PClBz

Table 1: Number of the variables used for PCA and CA statistical analyses. * - I-TEQ value

Statistical Analysis: Statistical Package 3.11g, Kovach Computing Service is used for the PCA and CA. PCA is used to classify the variables and elaborate relationships between them. The effect of CA is used to find the most correlated samples between. No transformation of the data is performed during the statistical analyses.

Results and Discussion

Principle component analysis (PCA) is used in order to give a better view of the similarity between the 21 samples considering their 36 variables which include the concentrations of PCDD and PCDF, PCB and PClBz.

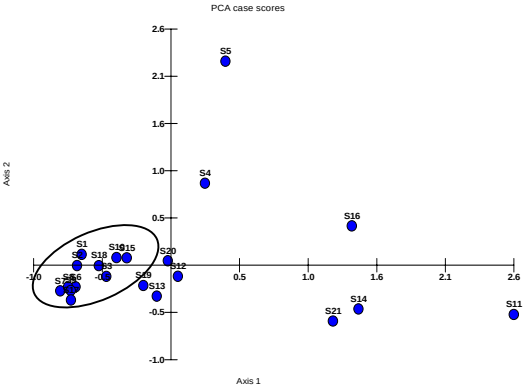


Figure 1: PCA score plot of 21 cases (samples) and 36 variables (PCDD/F, PCB and PClBz patterns).

One agglomerated group of samples, placed to the left side of the ordinate axis is observed in the proposed PCA score plots (Figure 1). These are the samples with lower concentrations of the investigated toxic compounds or samples treated with higher percentage of inhibitor. The samples on the right side and in the middle of the multidimensional space are samples without inhibitor and with higher amount of PCDD/F, PCB and PClBz i.e. sample number S4, S5, S11, S12, S13, S14, S16, S19, S20 and S21. CA is performed separately for that two groups of samples visualised by the PCA score plot. The first matrix used for CA include 10 cases and 36 variables and the second is present with 11 cases and 36 variables. The score variable plots are shown in Figure 2.

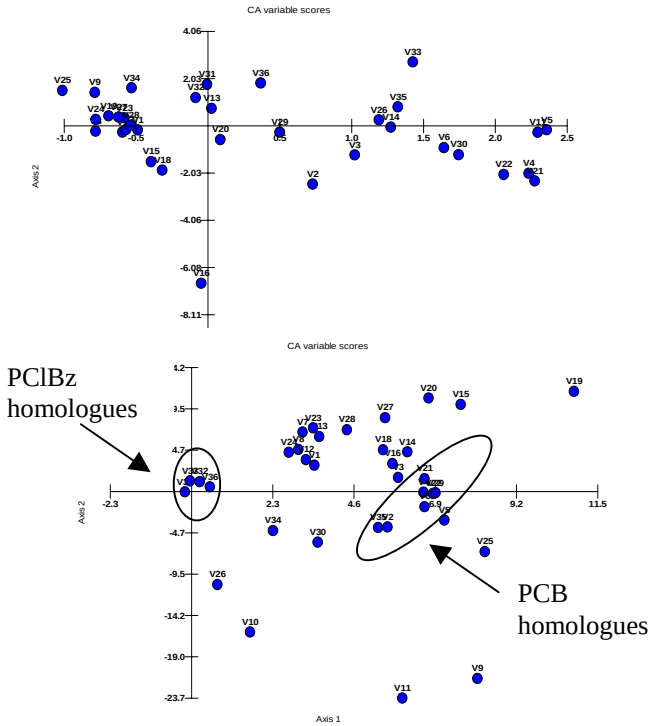
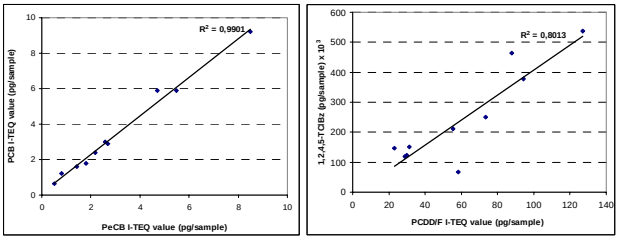


Figure 2: CA score variables plots for the samples with higher toxicity (A) and lower toxicity (B)

It is obvious that in score variables plot (A) most of the points are much closer to each other compare to plot (B) where the variable points are more spread in the multidimensional space. Some of the most interesting corresponding correlations are drawn in two dimension graphics in Figure 3.

A



B

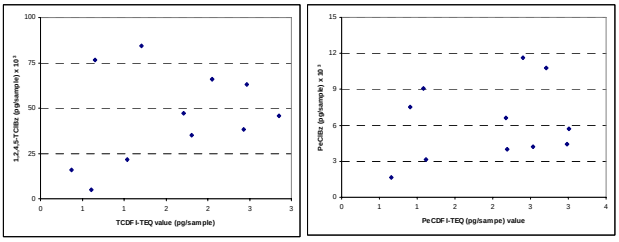


Figure 3: A- Correlation between couple points of score variables plot (A) of CA in Figure 2. V15 and V18; V13 and V32; V23 and V32; V24 and V34; B- Correlation between couple points of score variables plot (B) of CA in Figure 2. V23 and V32; V24 and V34.

A good correlation was found between chlorinated benzenes and chlorinated dibenzo-p-furans for the samples treated without inhibitor or with low percentage of inhibitor. According the precursor theory of PCDD/F formation a fusion of two chlorophenyl radicals result in PCB compounds. In a later steps that molecules can be oxidized and are thus potential precursors of PCDF [4]. The best indicator parameter between the investigated PClBz congeners is 1,2,4,5-TClBz. That isomer is also correlated with PCDD/F I-TEQ value. The best relationship between the chlorinated benzenes and PCB I-TEQ value, is found for PeCB.

For the samples treated with high percentage of inhibitors the above mentioned relationships are not observed (Figure 3 B). In score variables plot (B) of Figure 2 seems that PClBz and PCB homologues variables are placed further apart of each other. PCDD/F variables points are spread around the multidimensional space. The observed couples of variables in Figure 2 (B) belong to the same class of compounds.

Acknowledgments

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References

1. Kaune A., Lenoir D., Schramm K. W., Zimmermann, R., Kettrup A., Jaeger K., Ruckel H. G. and Frank F. (1998) Environmental Engineering Science 15, 85.
2. Blumenstock M., Zimmermann R., Schramm K. W. and Kettrup A. (2001) Chemosphere 42, 507.
3. Henkelmann B., Schramm K. W., Klimm C. and Kettrup A. (1996) Fresenius Z. Anal. Chem. 354, 818.
4. Tuppurainen K., Halonen I., Ruokojarvi P., Tarhanen J. and Ruuskanen J. (1998) Chemosphere 36, 1493.