Prediction of the Thermal Stability of PCBs Using their Physico-Chemical Properties and Comparison of the Results with the Levels in an Incineration Sample.

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Introduction

PCBs are emitted to the environment in flue gases and on fly ash during the incineration of municipal waste [1,2,3,4,5]. Although the precise reaction mechanism is not yet known, it is generally assumed that PCBs, as PCDDs and PCDFs are formed in the cooling zone of the incinerators by means of the so called *de novo* synthesis[6]. In order to obtain more information on the formation of PCBs in relatively low temperature regions (200-400°C), the thermo stability of PCBs was studied at 300°C. The relative congener distribution obtained from the thermal stability tests, compared to the congener distribution in a real incineration sample is expected to give an indication if the product composition is determind kinetically or thermodynamically during incineration. Because testing all 209 PCBs is not feasible from both an economical and time perspective, 20 tetra- through hepta- PCBs were selected for testing. This selection was made by using a fractional factorial design on the first four principal components of the multivariate statistical analyses of 47 physico-chemical properties of the PCBs[7]. In this way the 20 selected PCBs are covering the so called 'chemical space' of the PCBs as accurately as possible.
The data from the 20 selected 'training set' congeners can then be used to predict the thermo stability of the other PCBs from their chemical properties by means of the statistical tool partial least squares to latent variables (PLS). This approach has been successfully used in predicting the toxicity of PCDDs, PCDFs and PCBs by using multivariate quantitative structure activity relationships[8] and is expected to be also suitable for modelling the formation of PCBs.

Experimental

Ampoules of 1.2 ml (4.50-4.75 mm. id.) were filled with toluene washed sand. The different PCB congeners (100-750 ng) was added to the sand in toluene. The following PCBs were used as a trainings set in this study using the IUPAC numbers for the different congeners: PCB #41, PCB #51, PCB #58, PCB #60, PCB #68, PCB #78, PCB #91, PCB #99, PCB #104, PCB #112, PCB #115, PCB #126, PCB #143, PCB #153, PCB #169, PCB #173, PCB #184, PCB #188, PCB #190 and PCB #193. After evaporation of the solvent the glass ampoules were sealed in a gas flame. The ampoules were placed in an HP5890A GC-oven and heated to 300°C for 5 minutes. After cooling down to room temperature the ampoules were opened and an internal standard containing one ^{13}C labelled PCB at each chlorination level was added. The sand was transferred to a silica column containing H_2SO_4-silica, activated silica and Na_2SO_4 and eluted with 8 times the column volume of hexane. Before evaporation 40μl of tetradecane was added and before the GC injection a recovery standard containing ^{13}C labelled PCB #80 and #128 was added. The GC/MS analyses were carried out on a Fisons MD800 mass *spectrometer* coupled to a Fisons GC 8000 gas chromatograph using the selected ion recording (SIR)

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mode. 1µl of each sample was injected on a non-polar column (J&W DB-5, 60m, 0.32 id., 0.25 µm film thickness, Folsom, CA, USA) by means of splittless injection. Multivariate modelling was performed using the SIMCA-S 5.1 package (Umetri AB, Box 7960, S-907 19 Umeå, Sweden) on a PC operating in a Windows environment. The data was arranged as in Figure 1 and log transformed, centred and scaled to unit variance before modelling.
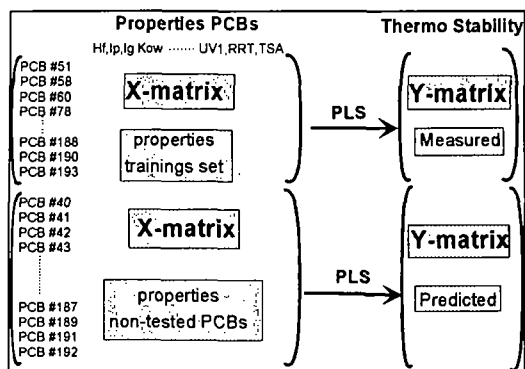

Figure 1. Outline of the data organisation

Results and discussion

The results of the thermal reaction after 5 minutes at 300°C in the sealed glass ampoule applied on sand are presented in Table 1. The results are presented as the percentage degradated compared to the amount applied on the sand. All 20 PCB isomers showed considerable degradation ranging from 60 up to 93%. Most of the original compound was transformed to PCDFs which is in agreement with the literature[9,10] . More stable with respect to thermal degradation were the PCBs #41, #126, #169, #184, #173 and #190. No strong relation between the stability and the degree of chloration was found and the thermo stability seems to be more dependent on the positions of the chlorine atoms than the number of chlorine atoms. It is however difficult to establish which specific chlorination pattern is more favourable for the thermal degradation.

Table 1. Degradation percentages after 5 minutes at 300°C in a sealed ampoule on sand.

PCB congener	Degradation %	PCB congener	Degradation %
PCB #41	72%	PCB #115	84%
PCB #51	92%	PCB #126	72%
PCB #58	93%	PCB #143	88%
PCB #60	87%	PCB #153	79%
PCB #68	83%	PCB #169	60%
PCB #78	89%	PCB #173	65%
PCB #91	87%	PCB #184	65%
PCB #99	88%	PCB #188	83%
PCB #104	92%	PCB #190	74%
PCB #112	89%	PCB #193	83%

The thermo stability data in Table 1 was further used to calculate a multivariate model as outlined in Figure 1. This model, consisting of 3 significant PLS dimensions (see Table 2 for specifics), was used to predict the thermostability of the 136 non tested tetra- through hepta- PCBs congeners. Although the calculated model was not perfect, and we would have liked to see a higher Q^2 value, the predicted values give a clear indication of the thermostability of the different PCBs. In order to further validate the predictions and to establish if there is a relationship between the predicted thermostability and the formation of PCBs during incineration, the predictions were compared with the relative congener distribution in a sample from waste incineration.The specifics of the analysis of the incineration sample are described elsewhere[4] and the data was recalculated to the relative distribution at each chlorination level,

e.g. the total per chlorination level was set to 100%. Also the degradation percentages were transformed into relative stability data by taking 100% minus the degradation percentages. These percentages were again normalised to 100% at each chlorination level.

Table 2. Statistics of the PLS model

	R^2X	R^2Y	Q^2_{int}
PC1	37.5%	33.8%	0.121
PC2	53.3%	56.2%	-0.215
PC3	76.2%	64.9%	0.103

In Figure 2 both the predictions and the real values of an incineration sample are presented for the tetra isomers as a bar diagram. Reasonable good agreement is achieved considering the problems with co-elution of different isomers and the uncertainty of the model. It is especially striking that the late eluting planar isomers PCB #77, #81, #78 and #79 are both high in the real fly ash as well as in our predictions in the far right of the diagram. Also on the other chlorination levels there is a reasonably good agreement between the predicted and real relative levels.
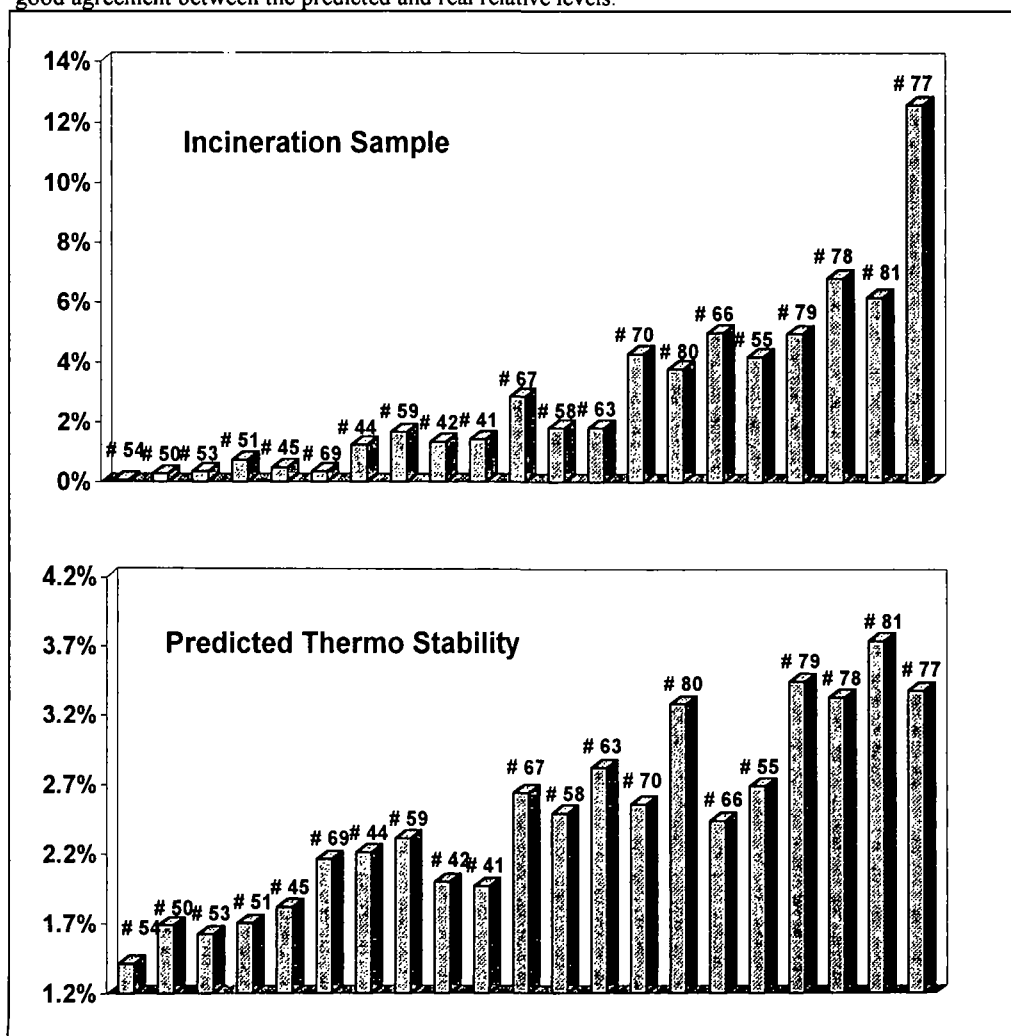

Figure 2. The predicted and measured relative levels of the tetra PCBs.

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Conclusions

The degradation of a training set containing 20 PCB congeners selected by means of a multivariate design on sand heated in a closed ampoule varied from 65 to 93 %. This data enabled the prediction of the thermostability of all 136 tetra- through hepta- PCB congeners by calculating a multivariate model using the physico-chemical properties of the PCBs. The predicted thermostability of the tetra- through hepta- PCBs was found to be in reasonable agreement with the relative PCB isomer distribution at each chlorination level in a real fly ash sample. Thus indicating that the thermo dynamic properties of the PCBs play a role in the formation and relative isomer distribution of these compounds during the *de novo* synthesis of PCBs during waste incineration.

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