

## Chromium as a potential catalyst in the thermal formation of chlorinated aromatic compounds

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### Introduction

Chlorinated aromatic compounds were detected in fly ash from municipal solid waste incinerators in the late 1970s <sup>1,2</sup>. It was later shown that this fly ash possess catalytic properties enhancing the formation of PCDD/PCDF also at moderate temperatures <sup>3</sup>. Copper is a well-known active oxychlorination catalyst in the Deacon process and is postulated to be responsible for this the low-temperature formation of chlorinated aromatics <sup>4</sup>. The catalytic activity of copper has also been demonstrated in both laboratory experiments and full-scale trials <sup>5-12</sup>.

However, copper is not the only metal that is an active oxychlorination catalyst. A substantial number of other transition elements also possess similar activity and interactions are well known <sup>13</sup>. It is therefore of interest to widen the scope to include the fly ash metal composition as a whole. The number of studies with other elements than copper is limited.

The element composition of municipal waste is not constant, but changing both between sources and over time. These variations could provide the means to study the influence from fuel composition on the thermal formation of chlorinated aromatics, and such studies have been attempted <sup>14</sup>. Unfortunately process related factors will hide correlations in the observation data, making this approach difficult. An experimental study can be more successful in providing information about the effect from fuel and fly ash composition <sup>15</sup>.

Previous investigations in Sweden of the influence from different separation schemes on waste fuel composition can provide data suitable for evaluating the link between element composition in the fly ash, catalytic activity and the formation of polychlorinated benzenes, phenols, dibenzo-*p*-dioxins and dibenzofurans <sup>16</sup>. Here we will attempt to re-evaluate the analytical results from a series of 16 trials with different waste fuels in the same combustion plant <sup>17</sup>.

### Materials and Methods

The data used in the present study were obtained from a series of previous investigations in a bio-fuel incinerator operated by AB Borlänge Energi, Sweden. Fractions of waste from households (separated at source) and specified industrial wastes were incinerated, with waste from forestry as a

reference fuel. These combustion trials were performed to determine the influence of different separation schemes on the operation and combustion conditions, together with the environmental emissions and characteristics of the residues. Here our focus is limited to the variation in composition of the fly ash, with regard to elements and trace organic contaminants.

Each combustion test was run for approx. 24 h. Grab samples of fly ash from the electrostatic precipitator were collected twice each hour and after mixing the composite was analyzed. Lead, cadmium and mercury were analyzed by atomic absorption spectroscopy. Other minerals and trace elements were generally analyzed by X-ray fluorescence spectroscopy. Chlorinated benzenes, phenols, dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) were analyzed by high-resolution gas chromatography and selected ion monitoring mass spectrometry. The analytical procedure was described in an earlier paper<sup>18</sup>.

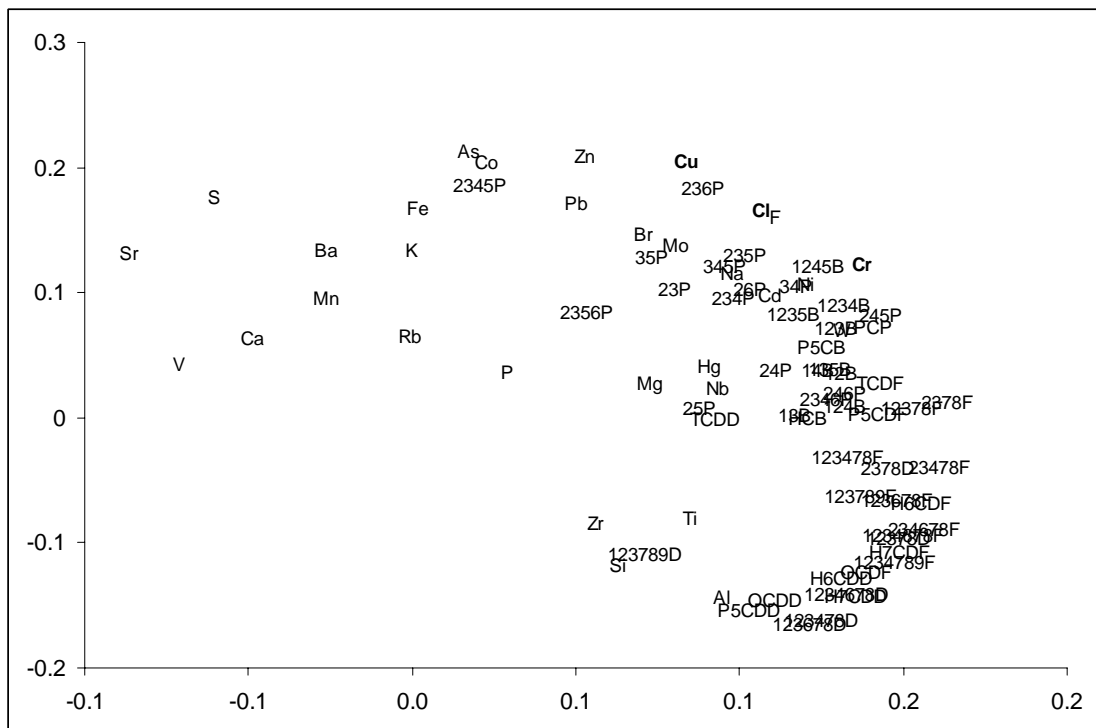
The correlation pattern was evaluated using principal component analysis<sup>19</sup>. A modified Box-Cox transformation to normality was adopted for each analytical variable<sup>20</sup>. All variables were standardised to zero mean and unit variance before the data analysis. The computations were run on a PC, using the software Unscrambler (CAMO Technologies, Inc.) and Matlab (MathWorks, Inc.).

## Results and Discussion

The fly ash samples were analysed for content of 32 elements (Al, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, K, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Si, Sr, Ti, U, V, W, Zn, and Zr), 16 chlorinated phenols (di-penta), 11 chlorinated benzenes (di-hexa) and 25 PCDD/PCDF (2378-substituted congeners and homologue groups). Values below the detection limit are treated as missing.

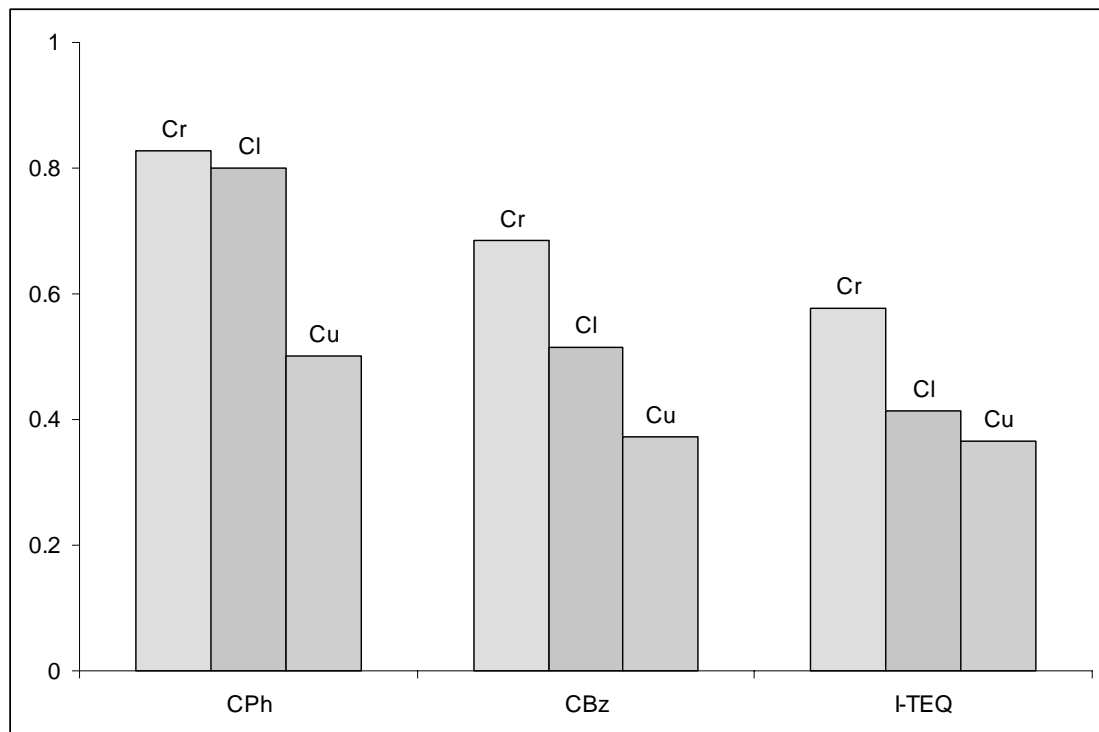
The correlation pattern between all of the 84 analytical variables can be visualised using principal component analysis (PCA). Uranium was excluded due to a large portion of measurements below the detection limit. A PCA model with two significant components, as determined by cross-validation, explains 56% of the total variance. The co-variation is thus substantial.

The variable contributions are displayed in the loadings plot, Figure 1. The first principal component explains 41% of the variance and some elements have a substantial contribution to this component, notably chromium, nickel and tungsten. Copper and chlorine are also positively correlated with the organic contaminants. The chlorinated aromatics with the largest contribution are some of the 2378-substituted PCDF congeners and in part this is due to their relatively high proportion out of the total number of analytes.



**Figure 1:** Variable loadings along the first two components of the PCA model. Copper, chlorine and chromium are highlighted.

The concentrations of nickel and tungsten were low compared to chromium and copper. Furthermore, chromium is rated as having a very high activity as an oxychlorination catalyst, possibly at a level comparable or superior to copper<sup>13</sup>. It is therefore of interest to focus more attention to this element. Figure 2 shows the correlation coefficients between these two elements and the sums of chlorinated benzenes, phenols and PCDD/PCDF expressed as I-TEQ (the international toxic equivalent quantity)<sup>21</sup>. The correlation coefficients for chromium are above the critical value of 0.574 and statistically significant at the 1% level.



**Figure 2:** Correlation coefficients between chlorinated aromatics and the elements chromium, chlorine and copper.

The reported findings seem to suggest that other metal catalysts and promoters than copper are present in the waste fuel. The correlations between the 52 chlorinated aromatic congeners and chromium are stronger for almost all of them compared to copper, and the same is true for a comparison with chlorine. A previous study on refuse-derived and packaging-derived fuels also reported on a correlation between chromium and the formation of chlorinated aromatics<sup>15</sup>.

We like to propose as a working hypothesis, that metals other than copper are of equal importance in the catalytic activity of the fly ash. Chromium, chlorine and copper are not statistically independent variables in this data set (the cross-correlations vary between 0.70-0.82). These results can therefore not be seen as conclusive regarding their relative importance.

Investigations into the thermochemistry of the Deacon process have provided insight about the limitations and constraints of possible metal catalysts<sup>22,23</sup>. A limited number of transition metals qualify for further investigations. Chromium is one of these metals, which may contribute to the *de novo* formation of chlorinated benzenes, phenols and PCDD/PCDF. We suggest that a statistical design of experiments strategy is applied to test the hypothesis put forward, to quantify the relative importance and interactions of the waste fuel components.

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