Chlorinated aromatics from combustion:

The influence of chlorine, combustion conditions and catalytic activity

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Presentation at the 8th International Congress on Toxic Combustion By-Products, Umeå, Sweden, June 17-19, 2003.

Background

- *De novo* formation of chlorinated aromatics in combustion was established long ago.
- Many attempts have been made to correlate observation data and establish links between plant operation, fuel composition, and the formation and release of chlorinated aromatics.
- Conclusive cause-effect relationships are however difficult to establish without experimentation.

Factors

- Early full-scale experimentally investigations highlighted the **temperature** dependence of both the formation and decomposition mechanisms for chlorinated aromatics.
- Early full-scale experimental investigations identified statistically significant quantitative relationships between the **chlorine** content of the fuel and the emissions of chlorinated aromatics.
- Low temperature (300-400 °C) **catalytic** formation is a third important factor.

Scope

- The present investigation was undertaken to assess the consequences of the installation of a boiler for energy recovery in an industrial plant.
- A review of the literature did not provide a sufficient basis to assess the possible effects and interactions of changes in combustion temperature, chlorine input and catalysis.
- Data were available from laboratory and pilot-scale investigations, but results from industrial plants were generally missing and interactions were not reported.

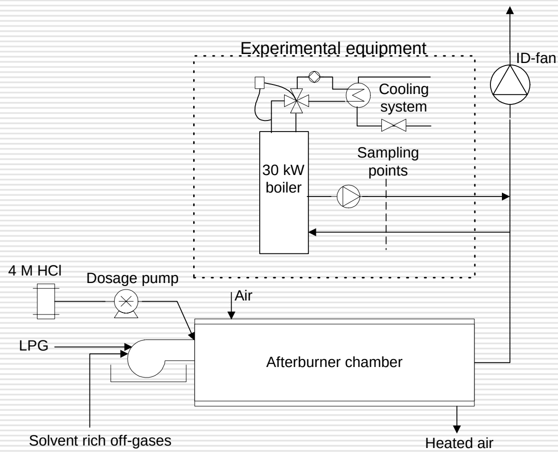
"Positive controls"

- A possible approach would be to simply evaluate the installation of a test boiler, without changing the normal operating conditions. However, such a study would,
  - neither provide information about the possible constraints for pollutant formation in this particular plant,
  - nor add the extra confidence provided to the evaluation by "positive controls".
- This extra validation was needed and the purpose of this study was thus expanded,
  - to also evaluate changes in chlorine input, combustion temperature and catalytic material.

Combustion device

- One of the afterburners in the steelworks of SSAB Tunnplåt AB, in the middle of Sweden.
- The afterburner is an air pollution control device and reduces the emission of organics from a paint drying oven, by combustion of the solvent rich off-gases.
  - Liquid petroleum gas (LPG) is used as the supplementary fuel to obtain suitable combustion conditions in the afterburner.
  - During the experiment a paint system based on PVC (polyvinyl chloride) was in use.

Experimental setup

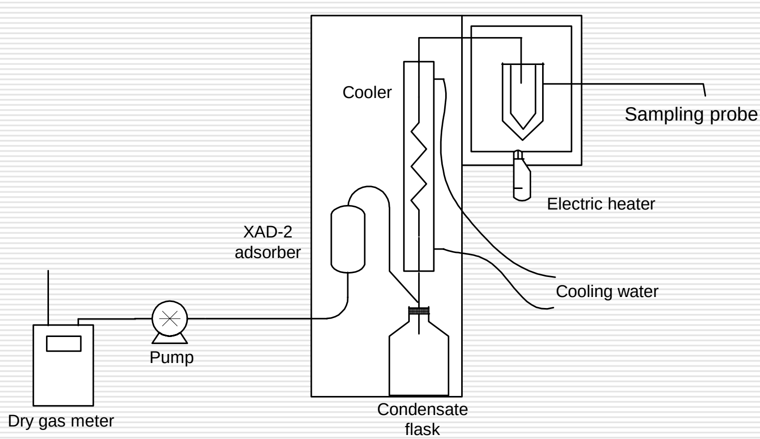


Domestic boiler, convective section and HCl dosage

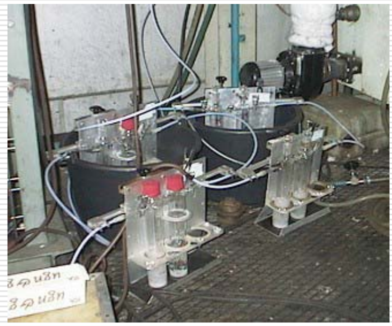
Exp. factors and responses

- Experimental factors:
  - Combustion temperature (post-flame), 705-750 ºC.
  - Addition of chlorine to afterburner, 4M HCl, 30 l/h => approx. 200 mg/m³ sdg (considerably less than MSWI).
  - Catalytic activity, mounting and removing copper lining sheet in the furnace tube.
- Measurement variables and responses:
  - O_2, CO and TOC (continuously).
  - HCl and Cl_2 (EPA Method 26)
  - Chlorinated benzenes
  - PCDD/PCDF (EN 1948)

The all-glass sampling train



Gas instruments and HCl/Cl_2-sampling train



Experimental design

- The experiment was set up as a factorial design with eight individual runs in a two blocks (one month in between).
- Each test run was 7 h, with 3 h for sampling and 4 h for pre-conditioning.
- Splitting the experiment into two blocks provided an opportunity to assess the influence of the operation time.
- The run order within each block was randomized.

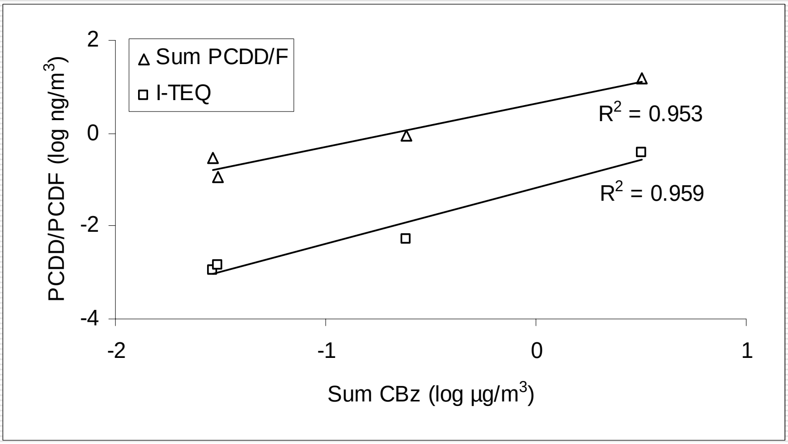
Data analysis

- Simple linear models were fitted to the data using multiple linear regression (MLR) and the effects to include were selected from normal probability plots.
- Analysis of variance (ANOVA) was used to assess statistical significance of the models and the various model parameters.
- Suitable variance stabilizing power transformations (Y^{α}) were found empirically.
- Software Unscrambler 7.6 (CAMO ASA, Oslo, Norway) and Statistica 6.1 (StatSoft Inc., Tulsa, OK, United States).

Settings and results

Run order	1	2	3	4	5	6	7	8
Experimental factors:								
Addition of chlorine (HCl)	Yes	No	Yes	No	No	Yes	Yes	No
Combustion temperature °C	705	705	750	750	750	705	750	705
Copper lining sheet	Yes	No	No	Yes	No	No	Yes	Yes
Block factor:								
Conditioning time (weeks)	0	0	0	0	4	4	4	4
Measurements, boiler inlet:								
Σ Chlorinated benzenes µg/m^3 sdg 16% O_2	2.2	0.43	1.2	0.75	0.029	0.48	0.24	0.011
PCDD/PCDF ng I-TEQ/m^3 sdg 16% O_2	n.a.	n.a.	n.a.	n.a.	0.0011	n.a.	0.0053	n.a.
Measurements, boiler outlet:								
CO mg/m^3 sdg 16% O_2	1460	1760	290	320	190	1740	280	1500
TOC mg C/m^3 sdg 16% O_2	16	21	7.1	7.7	3.4	15	4.0	16
HCl mg/m^3 sdg 16% O_2	259	8.0	280	19	4.0	187	175	5.0
Cl_2 mg/m^3 sdg 16% O_2	<1	<1	<1	<1	<1	<1	<1	<1
Σ Chlorinated benzenes µg/m^3 sdg 16% O_2	2.1	0.44	0.80	1.4	0.031	0.53	3.2	2.4
PCDD/PCDF ng I-TEQ/m^3 sdg 16% O_2	n.a.	n.a.	n.a.	n.a.	0.0014	n.a.	0.38	n.a.

Chlorinated benzenes as indicator parameters

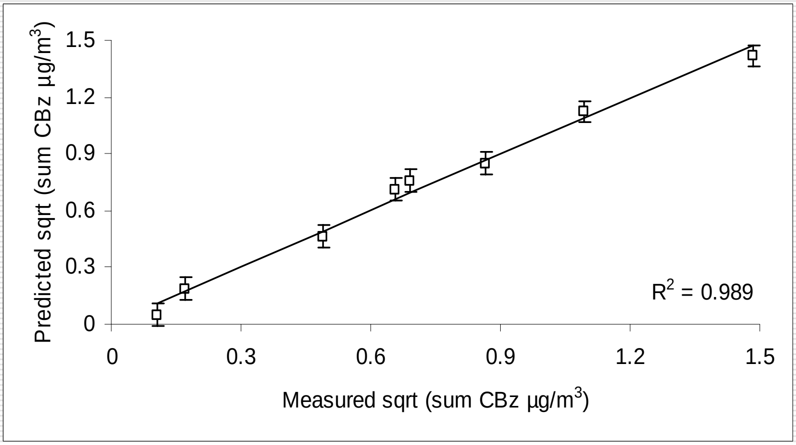


Linear model – boiler inlet

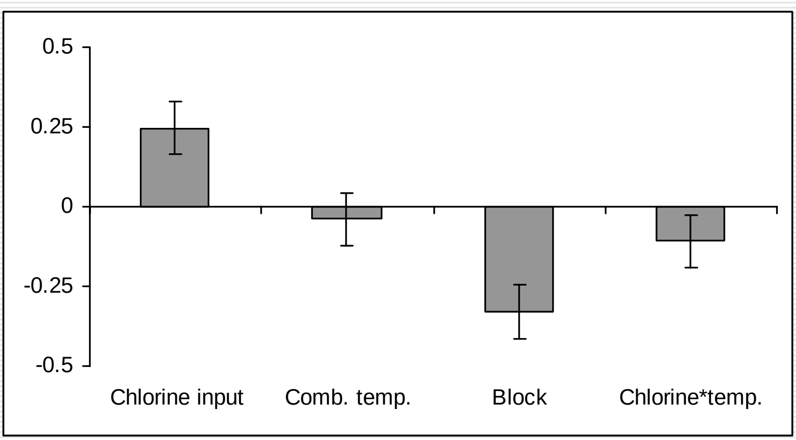
ANOVA of a linear model for chlorinated benzenes (square root transformation) in the boiler inlet, with the block factor describing variations in time.

Source of variation		SS	DF	MS	F	P
Model		1.462	4	0.365	66.11	0.0030
	Chlorine input	0.482	1	0.482	87.28	0.0026
	Combustion temp.	1.24E-2	1	1.24E-2	2.24	0.2310
	Block factor	0.873	1	0.873	157.94	0.0011
	Chlorine*temp.	9.38E-2	1	9.38E-2	16.98	0.0259
Residual		1.66E-2	3	5.53E-3		
Total		1.478	7	0.211		

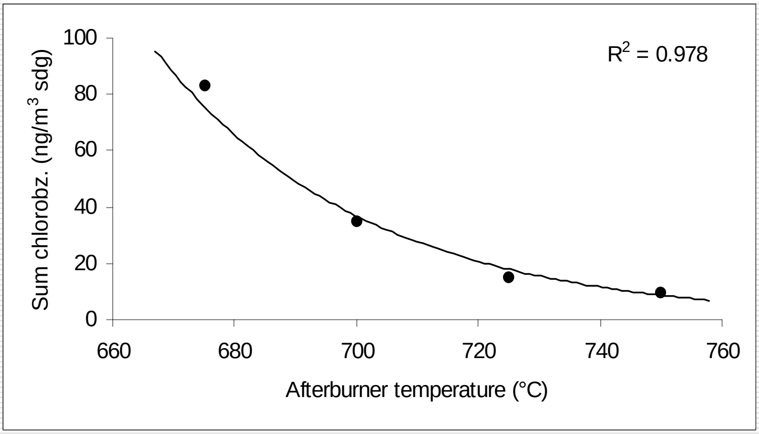
Linear model – boiler inlet: Predicted values



Linear model – boiler inlet: Coefficient estimates



Influence of temperature alone in a previous study



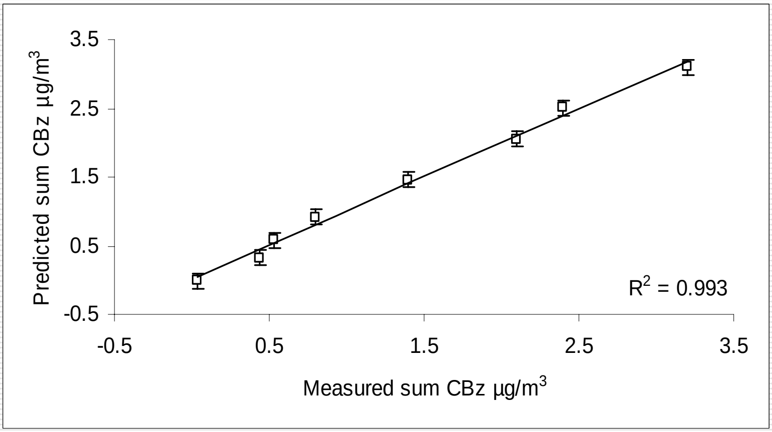
Öberg, T. *Optimization of an industrial afterburner*. Journal of Chemometrics 17, 5-8 (2003)

Linear model – boiler outlet

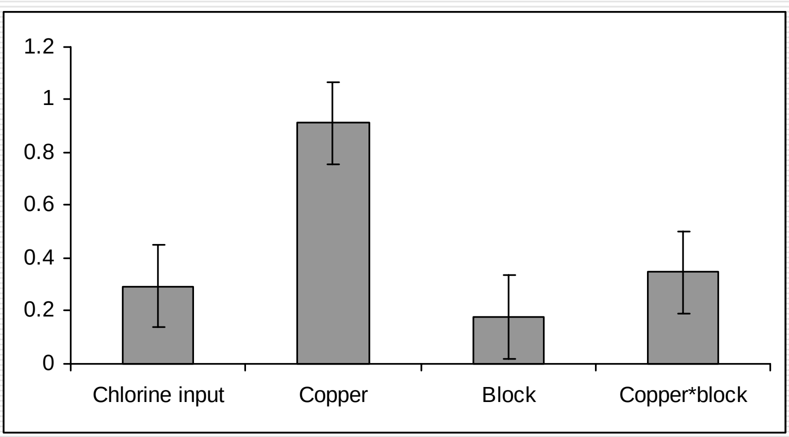
ANOVA of a linear model for chlorinated benzenes in the boiler outlet, with the block factor describing variations in time.

Source of variation		SS	DF	MS	F	P
Model		8.573	4	2.143	109.55	0.0014
	Chlorine input	0.696	1	0.696	35.56	0.0094
	Copper sheet.	6.659	1	6.659	340.40	0.0003
	Block factor	0.252	1	0.252	12.90	0.0370
	Copper*block	0.965	1	0.965	49.34	0.0059
Residual		5.87E-2	3	1.96E-2		
Total		8.631	7	1.233		

Linear model – boiler outlet: Predicted values



Linear model – boiler outlet: Coefficient estimates



Relative importance

- An evaluation of the formation and release of chlorinated aromatics from combustion, and other thermal processes, cannot neglect anyone of the three process factors investigated:
  - **Chlorine** input,
  - combustion **temperature** and
  - **catalytic activity** did all affect the outcome.
- The relative importance of each of these factors is dependent upon the constraints in the specific situation. It is therefore not possible to generally assign one as more or less important than the other.

Low risk

- In this study the purpose was to ensure that the installation of a boiler for energy recovery would not cause elevated emissions of chlorinated aromatics.
- The experiment demonstrated that this risk is probably low, since the presence of catalytic material or an increase in chlorine input is required for this to happen.

Copper as construction material

- Another conclusion is to avoid copper as construction material for convective surfaces.
- Copper is sometimes used in small and compact boilers in order to improve the heat transfer, e.g. in maritime vessels.
- It is not surprising that increased emissions of chlorinated aromatics have been observed from such boilers, when chlorine-containing fuels are fired. It was in fact this observation that gave us the idea to use a copper lining sheet as a test for the potential of catalytic low-temperature formation.

Full-scale experimentation

- A general problem with pure observation studies is that uncontrolled external factors can both hide real relationships and cause spurious correlations.
- It is therefore our view that cause-effect relationships should preferably be investigated using statistical design of experiments.
- The scaling-up of results from a laboratory environment to a full-scale technological process is not a trivial problem. We therefore believe that more such studies are necessary.

Acknowledgements

- This study was supported by AB Borlänge Energi and SSAB Tunnplåt AB.
- We thank Mats Hällström and Anders Åberg for valuable contributions in carrying out the experimental work.