

ADJUSTING THE OPERATION CONDITIONS OF WASTE INCINERATORS FOR
MINIMIZED DIOXIN FORMATION BY "IN-LINE" MONITORING OF
CHLOROBENZENS AND CHLOROPHENOLS

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ABSTRACT:

Experimental studies over the past two years in three waste incinerator plants on the correlation of dioxin formation to gasphase dioxin precursors resulted in a technique to describe a plants dioxin formation potential. More so, operating parameters of the combustion system could be elaborated to a minimized dioxin output. Low dioxin output can be continuously controlled by following first order parameter settings like temperatures, gas flows and air distribution in the furnace.

INTRODUCTION:

Formation of chlorinated hydrocarbons in waste incinerators is subject to extensive studies over the past 12 years. The conversion of a complex, not defined conglomeration of organic substances into gases and ash is not a process for detailed chemical consideration in respect to a detailed knowledge of reaction steps and kinetic calculations to describe the end products. Yet, the needs for destruction of various matter by incineration on one hand and the possible formation of toxic products in the gas and solid phase on the other hand drive analytical methods together with engineering to a better understanding and control of combustion processes.

Analytical methods for dioxine analysis of gases, liquids and solid samples was strongly developed over the last years to a state of the art technique. Today we may have information on dioxin contents of every imaginable matter ranging from dairy products to toilet paper.

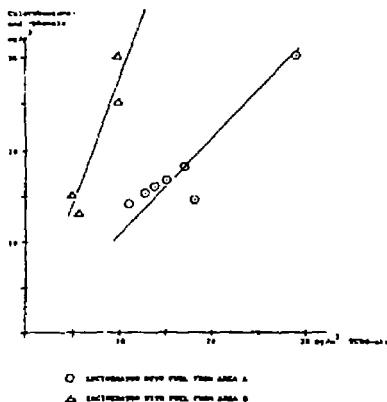
A drawback of all methods in dioxin analysis is the rather complicated sampling, extraction and measuring procedures that giving a too long lag of time between a dioxin sample and the information on its production rate. This problem starting with a long intergration time on the sampling routines, turn studies on the influence of individual parameters of an incinerator to its dioxin production capacity to time consuming and errorous

experiments.

The application of a newly developed mass spectrometer gas analyzer to raw gas in-line analysis allowed the development of a fast monitoring system to characterize dioxin formation condition in incinerators.

METHOD:

Halogenated aromatic hydrocarbons, especially CHC's can be seen as dioxin precursors or tracers when determined in the hot exhaust gases of incinerators. Experimental work on three different waste incinerator plants in Sweden and Germany could demonstrate a clear correlation between the sum of chlorinated aromatic hydrocarbons and the sum of the dioxin output. (Here is shown correlation characteristics of two furnaces).



Although the correlation is a complicated function and differing from plant to plant the

characteristic values $C = \frac{\sum c_i [\text{CHC}]}{\sum c_j [\text{TCDD}]} / c_1 / c_2 \rightarrow 0$ shows

to be a reproducible and characteristic number for each plant under study. More so, whenever the operating conditions of the incinerator were found for a minimum signal of the CHC's, a minimum level for the sum of dioxins was achieved. Minimum conditions are found by stepwise variation of the main parameters as input rates and gas flow rates, oxygen and carbon monoxide levels, temperature and air distributions in the boiler. With the mathematical tool of variational analysis invariable and sensitive parameters are worked out.

Interesting enough it was found that a minimum in carbon monoxide emissions is not associated with a minimum of CHC emissions and hence dioxin formation. See figure 4.

Variations of the amount of chlorine input of + 15 % weight to the boiler are increasing resp decreasing the the absolute CHC values

dramatically and consequently also the dioxin amount, but hardly influence the operating conditions as CO, O₂, furnace temperature etc. (See also figure 2)

EXPERIMENTAL:

A secondary ion mass spectrometer system was used for the CHC monitoring. This instrument equipped with a soft ionization unit, a quadropole mass selector and a sensitive detector with counting unit is capable of a mass range to 500 a.m.u. (atomic mass units) and a detection limit of 10 ppb. The use of the internal energy (ionization potential) of an ion beam as ionizing medium gives the advantage of superior sensitivity. The ionization potential is chosen so that the major constituents of the gas N₂, CO₂, O₂, H₂O are not ionized but act as a inert gas in elastic collisions. This condition reserves all ionizing power to molecules with energies lower than 11 eV (in our studies) i.e. all aromatic hydrocarbons. A second important condition is the non fragmental character of the ionization process leaving molecules with ionization potentials higher than 9 eV on their M⁺ peak otherwise producing M-X peaks where X is the atom with smallest bond energy to the core.

Being a portabel analyzer the instrument was mounted as near as possible to the extraction filter for the gas sample. The gases under study were transported in Teflon lines heated up to 180 °C and dustfiltered by a 2 micron filter unit. A absolute pressure controlled inlet system is transferring sample gas from the bypass stream at a flow rate of 0,2 cm³/min STP to the ionization chamber.

Molecules under study are selected from a library where all controlling parameters like atomic mass, resolution of the spectrometer, isotopic factors and the sensitivity range are defined. Isotopic pattern recognition is applied to identify the individual chloroaromatic compounds in the gas. See figure 1.

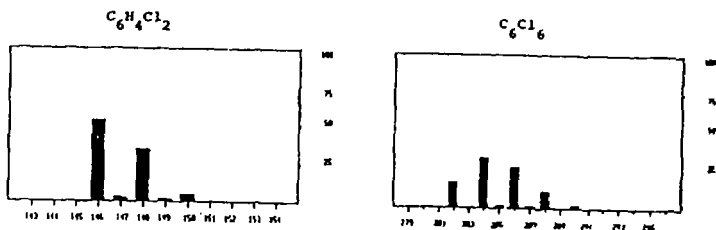


FIGURE 1

Correlation factors couple the sensivity ratios of chlorobenzenes to chlorophenols to a single calibration molecule. In our experiments $O^{16}O^{16}$ was chosen. Using a syntetic air bottle and the intensity of the $O^{16}O^{16}$ concentration the instrument zeroes and calibrates the whole number of selected molecules fast and accurate.

RESULTS AND DISCUSSIONS:

The response diagram:

Raw gas is extracted and feed to the analyzer via a bypass stream. The analyzer is set to a response time (T90 time) ≤ 5 sec and a sensitivity in the low ppb range.

In figure 2 the trend analysis or time dependence for the gas phase concentrations of 10 individual chlorinated compounds is shown. Time interval A shows a situation of standard waste input with normal operation of the boiler as seen by the "normal" signals. At point B one ton of risk materials carrying a higher chlorine content was substituted continuously in 30 minutes, i.e. to the normal waste. Gasphases of measured CHC+ show immediate response to the additional chlorine input.

467 / 007 - Trend-File Plotter Output
Changes of CHC output when increasing the chlorine input

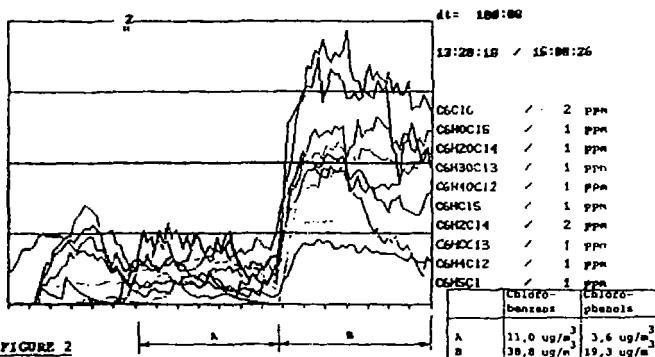


FIGURE 2

Intercrossings of the signals reflect the shift in the ppm distribution of Cl₁ to Cl₆ aromatic compounds:

	Time interval A rel. %	Time interval B rel. %
C ₆ H ₅ Cl	3,8	3,2
C ₆ H ₄ Cl ₂	1,4	5,3
C ₆ H ₃ Cl ₃	8,4	8,4
C ₆ H ₂ Cl ₄	23,8	14,7
C ₆ HCl ₅	10,8	13,9
C ₆ Cl ₆	24,5	20,9
C ₆ H ₄ OC1 ₂	9,7	4,4
C ₆ H ₃ OC1 ₃	7,3	9,1
C ₆ H ₂ OC1 ₄	4,6	7,9
C ₆ HOC1 ₅	5,7	12,2

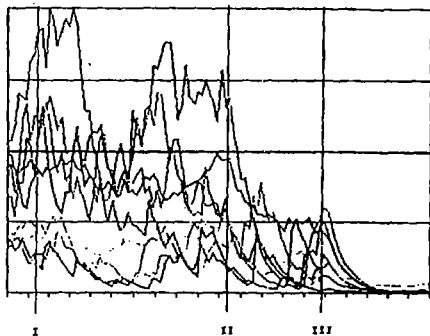
This fact was used to control for steady input conditions before an optimization procedure was started.

THE OPTIMIZING DIAGRAMS:

Starting from a constant input condition a step to step variation of the main furnace parameters is carried out. Concentrational changes of the measured compounds towards lower levels guides the direction of variations. Time scale for this optimizing process is determined by the inertia of the boiler to parameter variations. It was found that a boiler is optimized for minimum CHC output in about 20 hours. The optimizing procedure show reduction of CHC ranging from I to II and finally to III. See figure 3.

FNS AB optimizing program
Block A

dt: 64:39



CCl ₄	/	1 ppb
CCl ₂ F ₂	/	1 ppb
CCl ₃ F	/	1 ppb
CCl ₂ Br	/	1 ppb
CCl ₂ Br ₂	/	1 ppb
CCl ₂ BrCl	/	1 ppb
CCl ₂ BrF	/	1 ppb
CCl ₂ BrF ₂	/	1 ppb
CCl ₂ BrFCl	/	1 ppb
CCl ₂ BrF ₂ Cl	/	1 ppb
CCl ₂ BrF ₂ Cl ₂	/	1 ppb
CCl ₂ BrF ₂ Cl ₃	/	1 ppb
CCl ₂ BrF ₂ Cl ₄	/	1 ppb
CCl ₂ BrF ₂ Cl ₅	/	1 ppb
CCl ₂ BrF ₂ Cl ₆	/	1 ppb
CCl ₂ BrF ₂ Cl ₇	/	1 ppb
CCl ₂ BrF ₂ Cl ₈	/	1 ppb
CCl ₂ BrF ₂ Cl ₉	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₀	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₁	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₂	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₃	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₄	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₅	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₆	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₇	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₈	/	1 ppb
CCl ₂ BrF ₂ Cl ₁₉	/	1 ppb
CCl ₂ BrF ₂ Cl ₂₀	/	1 ppb

OPERATING SITUATION	O ₂	Primary air	Secondary air	Sum of CHC *)
I	9,5 %	30 500 m ³ /h	11 000 m ³ /h	28,7 ug/m ³
II	10,7 %	29 000 m ³ /h	14 000 m ³ /h	16,3 ug/m ³
III	12,1 %	30 000 m ³ /h	16 000 m ³ /h	8,8 ug/m ³

*) Summary of chlorobenzenes and chlorophenols

FIGURE 3

The elaborated minimas of CHC concentrations for three different boilers are in figure 4 shown as a function of O₂. Minima in CHC as well as the function [CHC] f(O₂) is different for every boiler.

Furnace A and B

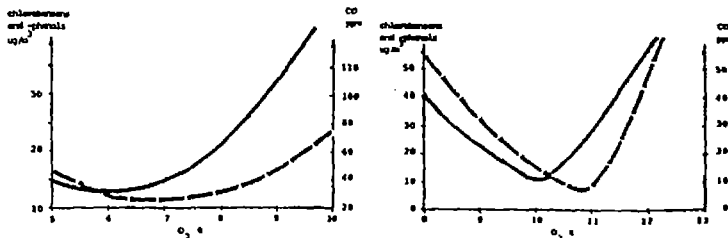


FIGURE 4:1

Furnace C

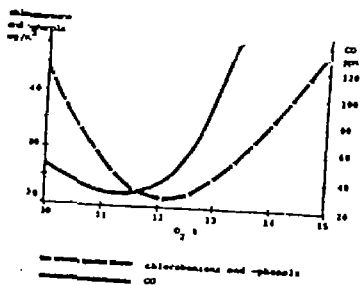


FIGURE 4:2

Again, the carbon monoxide minimum is not congruent with the CHC minimum and cannot be used for a minimum CHC output.

CONCLUSIONS:

Direct coupling of TCDD minima to CHC minima in the emission characteristic of waste incinerator systems was demonstrated. The coupling factors seem to be a function of furnaces mainly but further investigations have to support this conclusion. Relations of chlorobenzene and chlorophenols to two and trialemic species like CO, HCl, NO, NO₂ are observed but thermodynamically not yet understood. The use of fast and sensitive MS device in raw gas monitoring of dioxin precursors in the gasphase is a versatile tool in incinerator optimisation works.

ACKNOWLEDGEMENTS:

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