

Indicator parameters for PCDD/F in the flue gas of the hazardous waste incinerator at Leverkusen, Germany

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1. Abstract

In the flue gas of the hazardous waste incinerator (HWI) at Leverkusen, international toxicity equivalents (I-TE) could accurately be predicted from concentrations of hexa- and pentachlorobenzene (as shown before for another HWI) but also from the sum of tetrachlorobenzenes. This result is a further evidence for a wide applicability of the indicator parameter concept.

2. Introduction

Confirming earlier findings by Öberg and Bergström¹⁾, we showed that in the flue and stack gas of a hazardous waste incinerator the concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) were accurately predicted from the concentrations of either penta- or hexachlorobenzene²⁾. Slope and intercept of the regression equation depended on the type of the flue gas cleaning system. In order to find out whether slope and intercept also vary between plants and to extend the applicability of the indicator parameter concept, this paper presents data on a second HWI different from that investigated before.

A possible application of indicator parameters is their (on-line) measurement in the flue or stack gas of an incinerator and the subsequent estimation of the I-TE concentration using the regression between I-TE and the indicator parameter. Such application is currently under development employing laser-induced resonance-enhanced multi-photon ionization (REMPI) combined with time-of-flight mass spectrometry (TOF)³⁾. However, using REMPI-TOF higher chlorinated benzenes can only be determined in a two-colour experiment, i.e., two lasers are required for ionization. This makes the REMPI-TOF technique complicated and expensive. However, the lower chlorinated benzenes can be analyzed in an easier, one-colour experiment. Therefore, another objective of this study was to elucidate whether lower chlorinated benzenes can also be used as indicator parameters for PCDD/F.

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3. Materials and Methods

The hazardous waste incinerator consists of a rotary-kiln, a post combustion chamber operating at 1000–1200 °C, a heat recovery boiler, an acidic wet scrubber quenching the flue gas, two parallelly connected two-stage rotary wet scrubbers, a wet electrostatic precipitator and a selective catalytic reduction (SCR) unit. In September 1995, flue gas was sampled downstream of the heat recovery boiler at a temperature of about 420 °C while stack gas was sampled downstream of the SCR catalyst at a temperature of about 300 °C. Sampling was done isokinetically (according to VDI 2066, Blatt 1) using impingers filled with ethoxyethanol (VDI 3499, Blatt 3). Samples were divided, subjected to suitable clean-up procedures and analyzed by GC/HRMS (high-resolution mass spectrometry) for PCDD/F and by GC/MS (low-resolution mass spectrometry) for polychlorinated biphenyls (PCB), mono- to pentachlorophenol, mono- to hexachlorobenzene, polychlorinated *o*-, *m*- and *p*-terphenyl, and 20 polycyclic aromatic hydrocarbons.

Correlation and regression analyses were done using SAS procedures⁴⁾. If the data were not normally distributed (using a 0.10 significance level) Spearman's rank correlation coefficient rather than Pearson's product-moment correlation coefficient was computed. However, most of the data were normally distributed on a logarithmic scale.

Removal efficiencies (*RE*) were calculated according to $RE = 1 - (c_{\text{stack}}/c_{\text{flue}})$ where c_{stack} and c_{flue} are, respectively, stack and flue gas concentrations of simultaneous measurements.

4. Results and Discussion

In the flue gas, only three analytes significantly ($p < 0.01$) correlated with PCDD/F and I-TE, i.e. hexachlorobenzene (Cl_6Bz), pentachlorobenzene (Cl_5Bz) and the sum of tetrachlorobenzenes (Cl_4Bz) (Figure 1). Contrary to the results of our previous study on another HWI²⁾, I-TE did not correlate with chlorophenols or PCB. Quantification of the minimum and maximum concentration of Cl_5Bz was somewhat difficult because impurities were present in the chromatogram. Despite of this, the results demonstrate that higher chlorinated benzenes are good indicators for PCDD/F and I-TE. This is in agreement with findings for other incinerators. Furthermore, the applicability of the indicator parameter concept at full-scale incinerators could be extended to Cl_4Bz , but not to the mono- to trichlorinated benzenes. The latter may be due to losses of these volatile compounds during the sampling and analytical procedure which should therefore be improved. Then it seems possible that mono- and dichlorobenzenes can be identified as indicator parameters so that they can be monitored on-line by REMPI-TOF and permit an accurate prediction of I-TE. This perspective is also supported by the identification of lower chlorinated benzenes as indicator parameters for a laboratory-scale incinerator²⁾ using data from ref.⁵⁾. I-TE significantly ($p < 0.0001$) correlated with Cl_6Bz ($r = 0.872$), Cl_5Bz ($r = 0.927$), 1,2,3,4- Cl_4Bz ($r = 0.838$), 1,2,3,5- + 1,2,4,5- Cl_4Bz ($r = 0.891$), 1,2,3- Cl_3Bz ($r = 0.835$) and 1,2,4- Cl_3Bz ($r = 0.745$). The correlation of I-TE with 1,3,5- Cl_3Bz was considerably weaker ($r = 0.506$, $p < 0.05$) and there was no correlation with 1,3- Cl_2Bz and 1,4- Cl_2Bz . 1,4- Cl_2Bz did not react to PCDD/F in incineration experiments while 1,2- Cl_2Bz , which weakly correlated with I-TE ($r = 0.414$, $p < 0.05$), did form PCDD/F⁵⁾. This indicates that the principal cause of the correlation between PCDD/F and chlorobenzenes (PCBz) may be the formation of PCDD/F from precursors (such as PCBz). Indeed, precursor reactions have been found to dominate over *de novo* synthesis of PCDD/F⁶⁾.

A comparison of the regression results with those of another full-scale HWI and a laboratory-scale fluidized-bed incinerator shows that both slope and intercept of the regression line between

I-TE and PCBz are plant-specific (Table 1). This was expected because slope and intercept were also different at different sampling points within a given incinerator. However, certain improvements of the flue gas cleaning system, e.g. the addition of active carbon, may only change the intercept but not the slope²⁾.

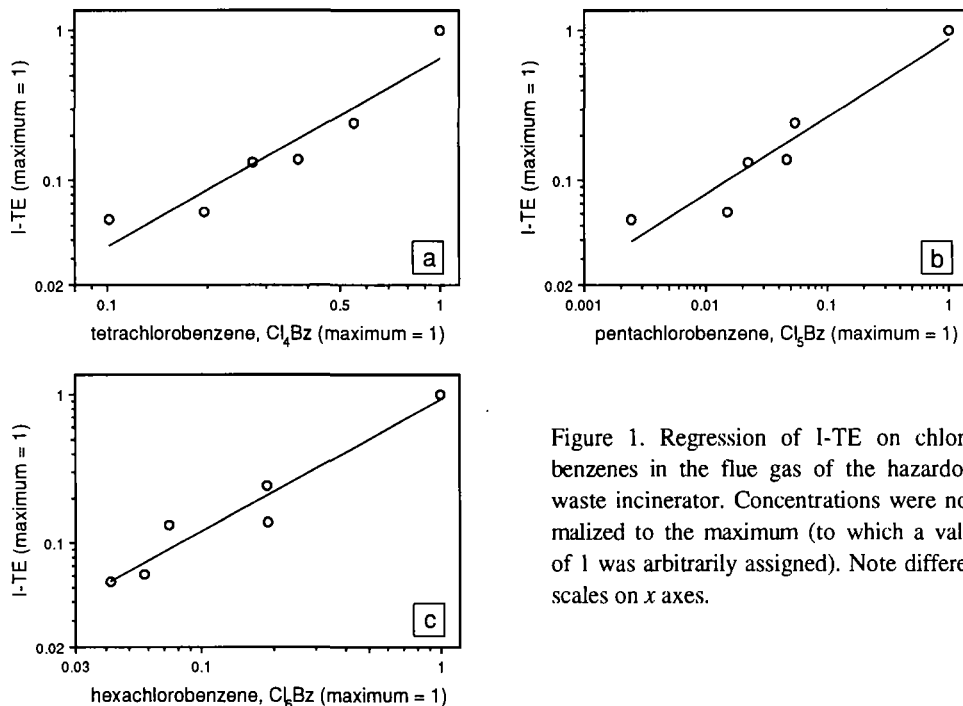


Figure 1. Regression of I-TE on chlorobenzenes in the flue gas of the hazardous waste incinerator. Concentrations were normalized to the maximum (to which a value of 1 was arbitrarily assigned). Note different scales on x axes.

In the stack gas, I-TE did not correlate significantly ($p < 0.01$) with any of the analytes (except PCDD/F homologues and congeners), not even with Cl_4Bz to Cl_6Bz , for which a significant correlation was observed in the flue gas. For the same experiment, removal efficiencies of Cl_4Bz to Cl_6Bz (ranging from -4.1 to 0.98) were typically lower than those of I-TE ($RE = 0.83$ to 0.9989). The removal efficiency of I-TE did not correlate with that of Cl_4Bz to Cl_6Bz so that removal characteristics for both groups of compounds are presumably very different. Negative removal efficiencies observed for Cl_4Bz to Cl_6Bz in one of the experiments imply that concentrations in the stack gas were slightly higher than those in the flue gas. This may be due to sampling and analytical errors. Furthermore, slightly higher stack gas than flue gas concentrations were only observed in a single measurement so that no general conclusion on the formation of PCBz in the flue gas cleaning system can be drawn.

The difference in the removal efficiency of PCDD/F and PCBz provides an explanation for the lack of correlation between these groups of compounds in the stack gas: The flue gas cleaning system effectively decreases PCDD/F concentrations but there is only a random effect on PCBz. Thus, the correlation between I-TE and PCBz, which is present in the flue gas, gets lost. According to previous investigations, this explanation does not hold for a wet scrubber and a wet electrostatic precipitator²⁾ but it may hold true for either the quenching unit or the SCR catalyst. Verification of this hypothesis requires simultaneous measurements of both PCDD/F and PCBz directly upstream and downstream of both devices.

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Table 1. Parameters of the regression equation $\log I\text{-TE} = a \log x + b$. I-TE and x were expressed in ng/m^3 . Contrary to Figure 1, the regression parameters were calculated for the original data.

x	a	b	r^2	p	n	reference
Cl_4Bz	1.3 ± 0.2	-3.0 ± 0.4	0.894	0.0044	6	this work
	0.77 ± 0.11	0.78 ± 0.14	0.756	< 0.0001	18	⁵⁾
Cl_5Bz	0.52 ± 0.08	-1.8 ± 0.2	0.912	0.003	6	this work
	0.92 ± 0.07	-2.8 ± 0.3	0.859	< 0.0001	29	⁵⁾
	0.40 ± 0.11	-0.07 ± 0.27	0.474	0.0022	17	downstream dry ESP ²⁾
Cl_6Bz	0.89 ± 0.12	-2.70 ± 0.3	0.932	0.0018	6	this work
	0.95 ± 0.10	-1.8 ± 0.3	0.761	< 0.0001	29	⁵⁾
	0.66 ± 0.18	-0.95 ± 0.50	0.471	0.0017	18	downstream dry ES P ²⁾

6. Conclusions

In the flue gas, Cl_4Bz to Cl_6Bz were good indicators of PCDD/F. This does not allow to use indicator parameters for stack emission monitoring but it still permits to use an on-line measurement of PCBz for optimization of incinerator operating parameters. Both intercept and slope of the regression of I-TE on PCBz are specific for a given incinerator and for a given sampling point within an incinerator. They cannot be deduced from other incinerators or sampling points. The correlation between PCDD/F and PCBz in the post furnace section of an incinerator may result from the formation mechanisms of both groups of compounds. At sampling points downstream of the formation section (e.g. within the flue gas cleaning system), this correlation can only be found if destruction or additional formation mechanisms (e.g. in an electrostatic precipitator) affect both groups of compounds in a similar proportion. These conditions were most likely not fulfilled for the HWI investigated here so that there was no correlation in the stack gas.

6. References

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