Indicator Parameters for Polychlorinated Dibenzodioxins and Dibenzofurans: Comparison of Different Incinerators

Andreas Kaune[1], Dieter Lenoir[2], Karl-Werner Schramm[2], Ralf Zimmermann[1],
Antonius Kettrup[1,2], Klaus Jaeger[3], H. G. Rückel[4] and F. Frank[4]

[1] Technische Universität München, Lehrstuhl für Ökologische Chemie und Umweltanalytik,
D–85350 Freising, Germany
[2] GSF – National Research Center for Environment and Health, Institute of Ecological
Chemistry, Ingolstädter Landstraße 1, D–85764 Neuherberg, Germany
[3] Bayer AG, ZF-D Zentrale Analytik, D–51368 Leverkusen, Germany
[4] SEF – Sonderabfall-Entsorgung Franken GmbH, D–91126 Schwabach, Germany

Introduction

As an extension of older observations by Oehme et al. (1) and Öberg and Bergström (2), we found that PCDD/F and I-TE values can be correlated with higher chlorinated benzenes (penta- and hexachlorinated benzene) present in the stack gas of a hazardous waste incinerator (HWI) (3). I-TE remained dependent on penta- and hexachlorobenzene even after the flue gas cleaning system of the facility was changed and active carbon was added downstream of the wet scrubber. However, the intercept of the regression line changed (4). The only example where chloro-benzenes could not be identified as indicator parameters for PCDD/F was a sampling point down-stream of a quench and a SCR catalyst of another incinerator. It seems that in the quench and/or in the SCR catalyst, the indicator parameter relation, which was still present upstream of these devices, was destroyed (5). Apart from penta- and hexachlorobenzene, tetrachlorobenzene was also found to be an appropriate indicator parameter for a second HWI (5). These chloroaromatic compounds occur in much higher concentrations in the effluents of the incinerators compared to PCDD/F. It is the ultimate aim of our investigations to measure chlorinated benzenes or phenols by on-line techniques like the recently developed resonance-enhanced multi-photon ionization time-of-flight mass-spectrometry (REMPI-TOF) (6). In the present paper, we compare the results of the regression analyses of PCDD/F on chlorinated benzenes and phenols for three facilities at four different flue gas sampling points, i.e. in the boiler, upstream and downstream of the electrostatic precipitator (ESP), and downstream of the wet scrubber. The objective of this paper is to determine if the regression results can be transferred from one incinerator to another. This would simplify the application of the indicator parameter concept.

Materials and Methods

The experimental measurements were obtained from three different German hazardous waste incinerators (A, B, and C). All facilities consist of rotary kilns with temperatures between 1000

and 1200 °C and a postcombustion chamber having a temperature in the range of 1000 to 1200 °C. The facilities differ in their cleaning system downstream of the boiler. All facilities have an electrostatic precipitator (ESP) for precipitation of the fly ash and wet scrubbers to absorb the acid gases but the locations of these devices are different for the three facilities. Facilities A and B have a ESP unit directly after the boiler, while facility C has a quenching device and a wet scrubber after the boiler, followed by the ESP. Facilities B and C have an additional SCR (selective catalytic reduction) unit. In facility B, the SCR is located after the wet scrubber and is followed by an adsorber. In facility C, the SCR is located downstream of the ESP.

The selected sampling locations are similar for all three facilities. A description of the sampling locations, denoted by numbers, is as follows:

1. In the flue gas upstream of the first flue gas cleaning device and at temperatures ranging from 400 to 600 °C. At facilities A and B, this sampling point was located in the boiler. At facility C, it was located between the boiler and the ESP where the temperature was 420 °C. Sampling location No. 1 will also be referred to as the boiler sampling point.
2. In the flue gas immediately upstream of the ESP at about 300 °C.
3. In the flue gas immediately downstream of the ESP at about 300 °C.
4. In the flue gas downstream of the wet scrubbers at about 90 °C.

PCDD/F as well as pentachlorophenol, pentachloro- and hexachlorobenzene were sampled according to the German VDI standards and guidelines (VDI 3499, Blatt 3) by isokinetic techniques using either XAD-2 resin or impingers filled with ethoxyethanol. Experimental details including analytical procedures can be found elsewhere (4,5,6). All concentrations were expressed in ng per m^3 of dry flue gas at 0 °C, 1013 hPa and 11 % O_2.

Results and Discussion

At the boiler sampling point (SP 1), measurements from facilities B and C can be described by the same regression equation, while the data points of facility A fall on a different regression line (Figure 1). The latter correlation lacks statistical significance probably due to a limited number of measurements ($n = 6$) and a relatively small concentration range. However, the slopes were nearly identical ($a = 0.66$ and 0.67) while the intercepts were different: $b = -2.7$ for facility A compared to $b = -4.6$ for facilities B and C (Table 1). Similarly, one regression equation describes the I-TE versus hexachlorobenzene data for facility A, and a different equation describes the data for facilities B and C. The difference in the slopes is larger than for Cl_5Bz. For pentachlorophenol (PCP) there were 19 measurements available for all three facilities and a good single correlation was obtained (Table 1 and Figure 2).

Significant regression equations were also observed upstream of the ESP (sampling point 2) for all three indicator compounds. Values are only available for two facilities (A and B) which can be described by the same regression line. However, the coefficients of determination (r^2) are relatively weak and less than those of the other sampling points (Table 1). The reason for the weak correlation is presently unknown. Sampling errors (e.g. resulting from turbulent rather than laminar gas flow and non-isokinetic sampling conditions) can be excluded.

Finally, significant correlation results were obtained for all three indicator parameters at sampling points 3 and 4 (Table 1).

Table 1. Regression of I-TE on pentachlorophenol (PCP), penta- (Cl_5Bz) and hexachlorobenzene (Cl_6Bz) at four different sampling Points (SP) of three incinerators. The regression equation used was: $\log$ I-TE $= b + a \log x$. The level of significance was $p < 0.05$ if not indicated as not significant (ns). The parameter values are given with their standard errors. The sampling points were: 1, boiler; 2, upstream of ESP; 3, downstream of ESP; 4, downstream of wet scrubber.

x	SP	b	a	r^2	n	HWI
PCP	1	-5.1 ± 0.60	0.87 ± 0.12	0.76	19	A, B, C
	2	-4.5 ± 1.3	0.90 ± 0.18	0.62	18	A, B [a]
	3	-3.3 ± 0.68	0.70 ± 0.091	0.83	14	A, B [a]
	4	-2.9 ± 0.52	0.64 ± 0.087	0.81	14	A, B [a]
Cl_5Bz	1	-2.7 ± 1.4	0.67 ± 0.32 ns	0.52 ns	6	A
	1	-4.6 ± 0.55	0.66 ± 0.11	0.79	12	B, C
	2	0.061 ± 0.60	0.35 ± 0.10	0.40	20	A, B [a]
	3	-2.4 ± 0.90	0.67 ± 0.13	0.63	18	A, B [a]
	4	-3.5 ± 0.55	0.64 ± 0.080	0.84	14	A, B [a]
Cl_6Bz	1	-8.0 ± 2.1	1.6 ± 0.43	0.74	7	A
	1	-7.0 ± 1.4	1.1 ± 0.28	0.62	12	B, C
	2	-1.8 ± 1.1	0.58 ± 0.16	0.41	21	A, B [a]
	3	-2.6 ± 1.1	0.62 ± 0.14	0.55	18	A, B [a]
	4	-4.2 ± 0.44	0.65 ± 0.057	0.91	15	A, B [a]

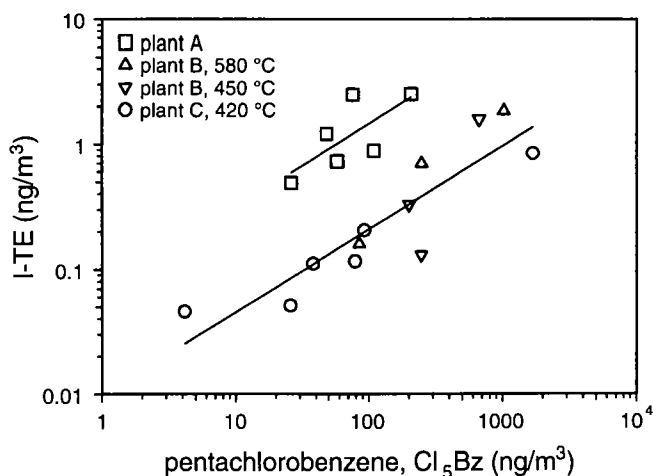[a] no data for incinerator C available

Figure 1. Correlation between I-TE values and pentachlorobenzene in the flue gas of the boiler.
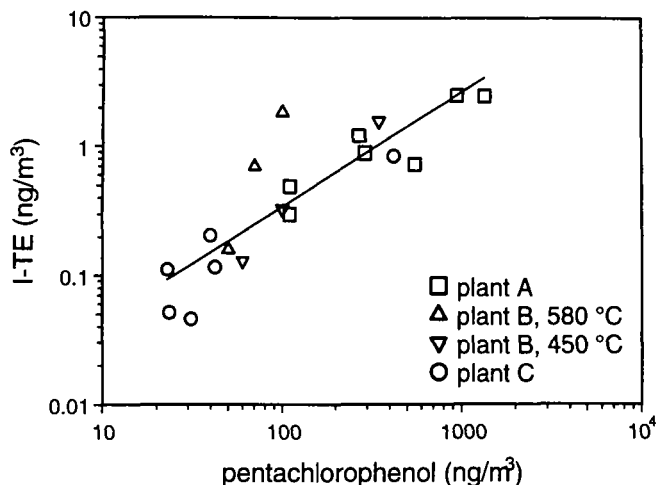
Figure 2. Correlation between I-TE values and pentachlorophenol in the flue gas of the boiler.

Conclusions

I-TE values can be predicted from concentrations of pentachlorophenol, penta- and hexachlorobenzene determined in the flue and stack gas of HWI. At sampling points which are similar for the different facilities the data points of these facilities either fall on the same regression line or on parallel regression lines which only differ by their intercepts. This finding simplifies the application of the indicator parameter concept and the transfer of results from one incinerator to another. For an incinerator which has not yet been investigated, the slope of the regression equation of I-TE versus the indicator compound can be taken from a similar sampling point of an already investigated incinerator. Only the intercept has to be determined. This typically requires much less measurements than the establishment of a full regression equation. These conclusions should be further verified by including more data for additional incinerators.

The correlations are also statistically significant for the boiler as the sampling point. This result infers that on-line measurement techniques of chlorobenzenes and chlorophenols may be used to control and optimize incinerators by direct primary measures.

References

1. Oehme, M.; Manø, S. and Mikalsen, A.; *Chemosphere* **1987**, 16, 143.
2. Öberg, T. and Bergström, J.; *Organohalogen Compd.* **1992**, 8, 197.
3. Kaune, A.; Lenoir, D.; Nikolai, U. and Kettrup, A.; *Chemosphere* **1994**, 29, 2083.
4. Kaune, A.; Schramm, K.-W.; Henkelmann, B.; Kettrup, A.; Nikolai, U.; Zimmermann, R. and Boesl, U.; *Organohalogen Compd.* **1996**, 27, 159.
5. Kaune, A.; Schramm, K.-W.; Kettrup, A.; Jaeger, K.; *Organohalogen Compd.* **1996**, 27, 163.
6. Zimmermann, R.; Boesl, U.; Weighardt, C.; Lenoir, D.; Schramm, K.-W.; Kettrup, A. and Schlag, E. W.; *Chemosphere* **1994**, 29, 1877.