

Pentachlorobenzene as indicator for PCDD/F emissions from a hazardous waste incinerator: Effect of using active carbon in the flue gas cleaning

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1. Abstract

In the stack gas of a hazardous waste incinerator, the concentration of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) correlated with that of pentachlorobenzene (Cl₅Bz) ¹⁾. In the present study, different types and points of addition of active carbon were investigated. At a given Cl₅Bz concentration (ranging from 5 to 600 ng/m³), lower NATO/CCMS toxicity equivalents (I-TE) were found when dry rather than moist active carbon was added downstream of the wet scrubber. Additionally adding active carbon into the first stage of the wet scrubber yielded the lowest I-TE values. In experiments of all three treatments, Cl₅Bz was a good indicator of PCDD/F and I-TE. This is a further strong evidence for the validity of the indicator parameter approach.

2. Introduction

Stack emissions of PCDD/F from the hazardous waste incinerator (HWI) investigated were drastically reduced by improving primary measures and by using active carbon in the flue gas cleaning process ²⁾. It was, however, not always possible to comply with the emission limit of 0.1 ng I-TE/m³. Thus, additional measures were necessary to reduce PCDD/F concentrations in the stack gas to values well below the emission limit. To achieve this goal, experiments with different types of active carbon (dry and moist) and with addition of active carbon at different points of the flue gas cleaning system were performed and are described in this contribution.

The results were also used to continue the investigation of indicator parameters for PCDD/F. Recent investigations showed that PCDD/F concentrations in exhaust gas and fly ash of waste incinerators are correlated with those of chloroaromatics (indicator parameters), e.g. chlorinated benzenes and phenols ^{1,3,4)}, chlorinated biphenyls ¹⁾ and chlorinated naphthalenes ⁵⁾. As a conse-

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quence, the PCDD/F emission can be estimated if the concentration of at least one of the above mentioned indicator parameter compounds in the flue gas and the respective indicator parameter relation is known. Recent developments in the field of laser-based on-line analytical techniques (resonance-enhanced multi-photon ionization/mass spectrometry, REMPI/MS^{6,7)} promise the capability of real-time, on-line detection of e.g. chlorinated benzenes and phenols. Therefore, the investigation of indicator parameter relations is of particular importance. The REMPI/MS approach is already applied for real-time measurements of automotive exhaust gas. On-line monitoring of PCDD/F indicator parameters in hazardous waste incinerator exhausts is a field of current research^{8,9)}.

At the HWI investigated, Cl₅Bz was the best indicator parameter from which I-TE levels could most accurately be estimated¹⁾. When active carbon was added downstream of the wet scrubber, the slope of the regression line of I-TE versus Cl₅Bz remained nearly unchanged but the intercept decreased by more than a factor of 10. Another objective of this study was, therefore, to investigate the effects of different types and points of addition of active carbon on the relation between I-TE and indicator parameters.

3. Materials and Methods

The hazardous waste incinerator consists of two rotary kilns, a post combustion chamber, an energy recovery boiler, a two-stage electrostatic precipitator (ESP), a two-stage wet scrubber, a condensing system and a wet ESP. Details can be found elsewhere¹⁾. In the stack gas (sampling point SP5 in¹⁾) samples were taken isokinetically according to VDI 3499, Blatt 5 using XAD-2 resin. Clean-up and analytical procedures were similar to those described in reference¹⁰⁾.

Downstream of the wet scrubber, active carbon was added into the gas stream in an aqueous suspension („moist“ active carbon) or by using compressed air („dry“ active carbon). The latter is technically more difficult and is associated with a relatively high risk of fire. In addition to adding moist active carbon downstream of the wet scrubber, in some experiments active carbon was added in aqueous suspension into the first stage of the wet scrubber. These measurements were performed in November and December 1994. From November 29 to December 14, 1995, a comparison between active carbon addition into the first and the second stage of the wet scrubber was made (3 measurements each). Concentrations were expressed in ng per m³ of dry air under standard conditions at 11 % O₂.

4. Results and Discussion

Figure 1 is an up-dated version of the regression of I-TE on Cl₅Bz¹⁾. Four additional measurements were included in which moist active carbon was added downstream of the wet scrubber. They well fit to the established regression line and support the conclusion that adding active carbon did not change the slope but the intercept of the regression equation.

At a given concentration of Cl₅Bz, I-TE values were lower when active carbon was added with compressed air („dry“) rather than in an aqueous suspension („moist“) and even lower when active carbon was additionally added into the first (acidic) stage of the wet scrubber (Figure 2). This effect may result from the different total adsorption capacity of the active carbon used. For all three treatments, the regression between I-TE regressed and Cl₅Bz was significant (0.05 level of significance, $p < 0.05$) despite the relatively small numbers of observations (n was 8, 5 and 5, respectively). Also, the regression lines of the three treatments were well separated in the concentration range considered.

The addition of active carbon directly into the first stage of the wet scrubber was most effective in reducing I-TE levels and yielded I-TE values well below the limit value. This treatment, however, produced severe side effects on mercury emissions. Hg concentrations were below the detection limit during the first 24 h of the experiments but then they increased quickly and reached values above the emission limit ($50 \mu\text{g}/\text{m}^3$). This side effect was reproducible but could be avoided by additional technical measures or by addition of active carbon into the second (neutral to slightly alkaline) stage of the wet scrubber. For the latter treatment, I-TE was $0.06 \pm 0.02 \text{ ng}/\text{m}^3$ ($n = 3$) and was not significantly different from the I-TE values obtained by addition of active carbon into the first stage of the scrubber (I-TE = $0.04 \pm 0.01 \text{ ng}/\text{m}^3$, $n = 3$). Thus, both treatments were similarly effective in removing PCDD/F.

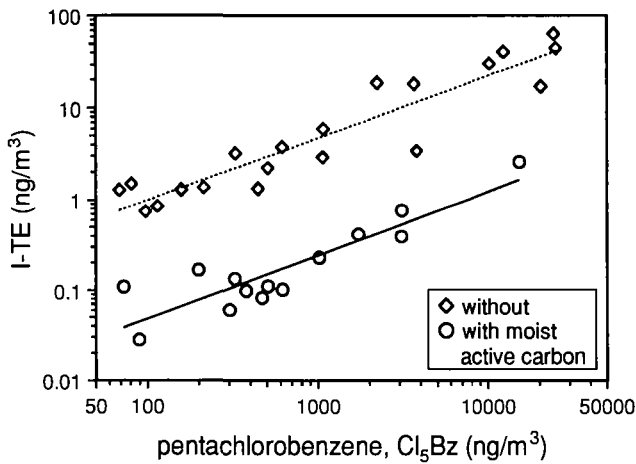


Figure 1. Relation between I-TE and Cl_5Bz without and with addition of active carbon. Active carbon was added as an aqueous suspension downstream of the wet scrubber.

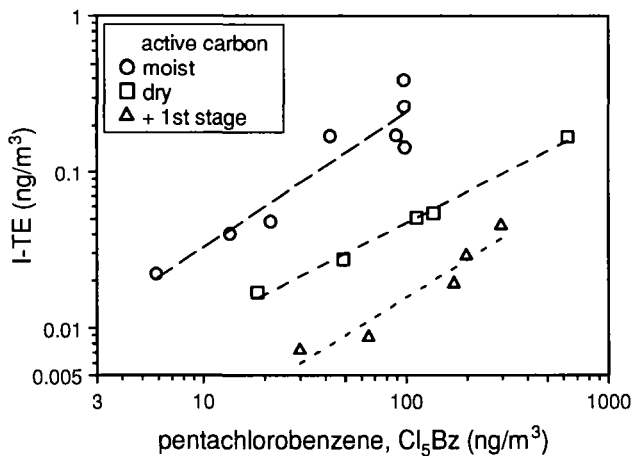


Figure 2. Relation between I-TE and Cl_5Bz when moist or dry active carbon was added downstream of the wet scrubber and when moist active carbon was additionally added to the first stage of the wet scrubber.

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5. Conclusions

Due to possible side effects mercury emissions should be monitored when active carbon is added into the first (acidic) stage of a wet scrubber which is currently becoming a common practice in many incinerators to reduce I-TE levels.

Changing an incinerator's flue gas cleaning device changes the relation between PCDD/F and chlorobenzenes. An application of the indicator parameter concept, i.e. the estimation of I-TE from (on-line) measurements of pentachlorobenzene, requires a knowledge of the type and operational state of the flue gas cleaning system. The same regression equation of I-TE versus chlorobenzenes can only be used for the same sampling point of a given incinerator and for a given set-up of the flue gas cleaning system.

6. References

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