MEASURING DIOXINS' PRECURSORS - A WAY TO ENSURE A CLEANER ENVIRONMENT

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Introduction

Incineration is a common method for treatment of municipal and hazardous wastes as the volume of the waste is considerably reduced and toxic substances and non-hygienic contents are decomposed, immobilized or trapped in the residues. In the flue and stack gas of municipal (MSWI) and hazardous waste incinerator (HWI) the so-called products of incomplete combustion (PICs), which are persistent and extremely toxic (polychlorinated dibenzodioxins - PCDDs, polychlorinated dibenzofurans - PCDFs, polychlorinated biphenyls - PCBs), can be detected.

Efforts were done to develop robust screening techniques to simplify the determination of the concentration of dioxins. There are essentially three screening strategies for the prediction of the I-TEQ of a sample of stack gases[1]:

(1) emission of a surrogate chemical (i.e. a compound other than PCDDs and PCDFs) can be measured in stack gases and correlated against corresponding of PCDDs and PCDFs;

(2) if a single PCDD/F congener can be identified, which bears a predictable relationship to the I-TEQ of the sample, then following sample collection, subsequent cleanup and analysis can be targeted with this simple congener;

(3) the I-TEQ can be measured directly with analytical screening techniques, which use certain enzymes (e.g. immunoassay).

The determination of the surrogates can be performed with higher precision than full dioxin sampling and analysis. Experimental studies revealed that some chlorophenols and all chlorobenzenes are in a good correlation with dioxins, whereas chlorinated benzenes have a higher predictive value than chlorinated phenols.

The goal of this work is to summarize the results of the experimental efforts done to find the correlations especially between chlorobenzenes and dioxins and to reveal the qualitative findings and quantitative correlations obtained by different authors. The experimental data published but not correlated in the literature were used to obtain original dependencies of PCDD/Fs on different surrogates[2].

Methods and Materials

The conventional measurement methods for dioxins (based on HRGC/HRMS) are time consuming and need high skills and costs; even a new proposed method, which drastically reduces the operation time, hazardous solvent consumption and thus, the cost, do not provide on-line real-time results[3]. The development of the applied mobile resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS) made the on-line detection of surrogate for PCDD/F in the flue gas of incinerators possible. This technique allows a highly selective, sensitive and fast detection of the surrogates, but its sensitivity is decreasing when the degree of the chlorination increases[4].

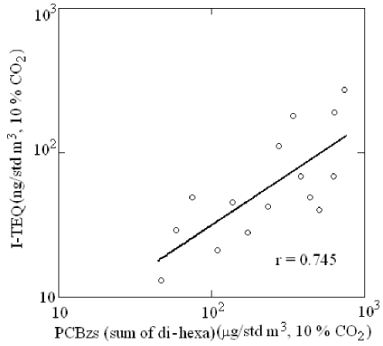

Figure 1. Regression of I-TEQ on polychlorobenzenes (sum of di-hexa)

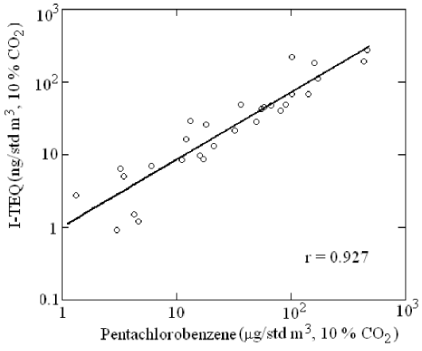

Figure 2. Regression of I-TEQ on pentachlorobenzene

Results and Discussions

International toxicity equivalent (I-TEQ) can be satisfactory predicted using either the total amount of polychlorobenzenes (fig. 1), or congeners (hexa-, penta-, tetra- or tri chlorinated) expressed either as sum of, or as individual isomers. I-TEQ can be determined with good accuracy using dichlorobenzenes (the most appropriate is 1,2-Cl2Bz) or monochlorobenzene. For indirect on-line measuring of the I-TEQ MCBz is the best-suited surrogate. Original correlations were obtained using data published by Fängmark[5]. According to that data, higher chlorinated benzenes can be used as good surrogates for dioxins. Between the congeners of polychlorinated benzenes, the most suitable surrogate seems to be pentachlorobenzene (fig. 2). There are differences between the usability as surrogates of the isomers. The least stable thermodynamically isomers in a homologue group are the most promising indicator parameters. I-TEQ correlates better with 1,2,3- (r = 0.835) than with 1,2,4- (r = 0.745) or 1,3,5 - trichlorobenzene (r = 0.506) (the correlation between I-TEQ and 1,2,3-trichlorobenzene is shown in fig. 3 as an example).

An interesting way to express the burden of organic compounds in parts of gram of compound per mega Joule of energy produced was used by Andersson & Marklund[6]; in this way the influence of different load levels of the biofuel and gas dilution is eliminated. Using Anderson's & Marlund experimental data, original correlations between I-TEQ and the sum of di-, tri-, penta and hexachlorinated benzenes were obtained in this study. I-TEQ value can be foreseen with a satisfactory

accuracy after the reactor (r = 0.806), respectively in the convector (r = 0.839). As an example, the correlation between I-TEQ and the mentioned PCBzs in the convector is shown in fig. 4.

The relationship between PCDD/F and indicator parameters is plant-specific and depends on formation and destruction processes downstream of the combustion chamber. It therefore also depends on the type of flue gas cleaning system. However, it seems that for many incinerators a reasonably accurate linear regression equation can be derived.

It is rather difficult to compare the different correlations or experimental data published, even when using the same surrogate, due to different types of incinerators and fuel, cleaning devices, different sampling points and even different ways to normalize the data (dry gases in standard conditions and 10 % CO_2, 11 % O_2, 13 % O_2 or unspecified) used.

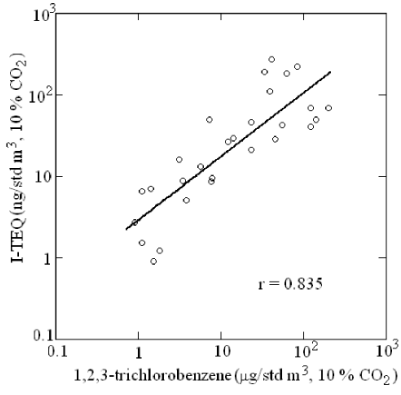

Figure 3. Regression of I-TEQ on 1,2,3-trichlorobenzene

The experimental studies proved that between some organic compounds, which could be used as surrogates and dioxins there is a functional relationship. This correlation, which allows the determination of the amount of dioxins (or the I-TEQ) in the emissions, depends on the incinerator, fuel used and flue gas' cleaning devices. However, a good agreement was found between the existent correlations of I-TEQ in the stack gas and monochlorobenzene in the flue gas[2] (fig. 5).

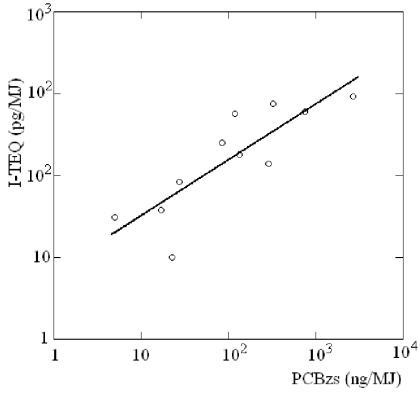

Figure 4. Regression of I-TEQ on PCBzs in the convector

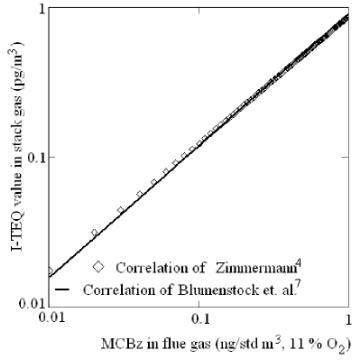

Figure 5. Comparison of the correlations for relative concentrations of monochlorobenzene in the flue gas and the I-TEQ in the stack gas[2]

The original part of this work is a cover-up of the scientific literature dedicated to the possibility to replace the determination of dioxins with some surrogates to characterize the emissions from combustion processes.

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References

1. Fiedler, H., Lau, C., Eduljee, G. (2000). Waste Manage. Res. 18, 283
2. Lavric E.D., Konnov A.A. and De Ruyck J. (2002) Indicator parameters for dioxins in incineration - a survey. Submitted.
3. Urano, K., Kato, M., Nagayanagi, Y., Saito, Y., Aono, A., Nagata, J., Syudo, H. (2001) Chempsphere 43, 425
4. Zimmermann, R., Heger, H.J., Blumenstock, M., Dorfner, R., Schramm, K.-W., Boesl, U., Kettrup, A. (1999) Rapid Communications in Mass Spectrometry 13, 307
5. Fängmark, I., van Bavel, B., Marklund, S., Strömberg, B., Berge, N., Rappe, C. (1993). Environ. Sci. Technol. 27, 1602
6. Andersson, P., Marklund, S. (1998) Chemosphere 36 (6), 1429
7. Blumenstock, M., Zimmermann, R., Schramm, K.-W., Kettrup, A. (2001). Chemosphere 42 (5-7), 507