

Application of a PCDD/PCDF Immunoassay for the Determination of TEQ in Fly Ash - a Comparison with GC/MS data

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Introduction

In environmental samples such as emissions of waste incineration polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are present as mixtures. The toxicological assessment of the emissions is based on the 2378-TCDD toxicity equivalents (TEQs). Therefore, calculation of these values requires the analytical determination of all 2,3,7,8-chlorosubstituted PCDDs and PCDFs which is time consuming and expensive if conventional methods are used. Rapid methods such as enzyme immunoassays (EIA) could be helpful for the screening of large numbers of samples.

Previous work toward EIA analysis of PCDDs and PCDFs [1-3] relied on an immunoassay which demonstrated useful sensitivity and TEQ screening capability, but was not developed commercially and is therefore not widely available. In the present study, a commercially available and more sensitive EIA [4] was used. This EIA has low picogram sensitivity and specificity appropriate for TEQ measurement. In the present study, EIA responses of 25 fly ash samples were determined after a rapid oxidation step performed on the crude toluene extracts. TEQ values were measured using the classical GC/MS method with samples subjected to the full clean-up procedure. Sensitivity and reliability of the EIA method were evaluated by comparing the two data sets.

Materials and Methods

The clean-up of the fly ash samples for GC/MS was based on an in-house routine method [5]. Calculation of TEQ values was based on I-TEFs [6].

Sample preparation for the EIA analysis included 3 h acid leaching of the fly ash with 1 M hydrochloric acid followed by Soxhlet extraction with toluene. An aliquot of this extract was reduced in volume and treated with concentrated sulphuric acid containing ca. 7 % (w/w) sulphur trioxide. The mixture was extracted with n-hexane and redissolved in methanol containing 0.1 % (w/w) Triton X-100. An aliquot of 10 μ L was used for the EIA.

Results and Discussion

Figure 1 shows the EIA response values plotted against the TEQ values as calculated from single congener concentrations measured by GC/MS. The correlation coefficient for these 25 samples is 0.98. Table 1 shows that the cross reactivities of the EIA used correlate with the I-TEF values of PCDDs and PCDFs. Based on Table 1, some nontoxic PCDDs and some coplanar PCBs could cause interferences, but the levels of these compounds in the current samples are unknown. The discrepancies between the two data sets can be explained partly by the fact that the cross reactivities of the 2,3,7,8-chlorosubstituted PCDDs and PCDFs in the EIA differ slightly from the I-TEFs (e.g. 12378-PeCDD and 23478-PeCDF, see Table 1).

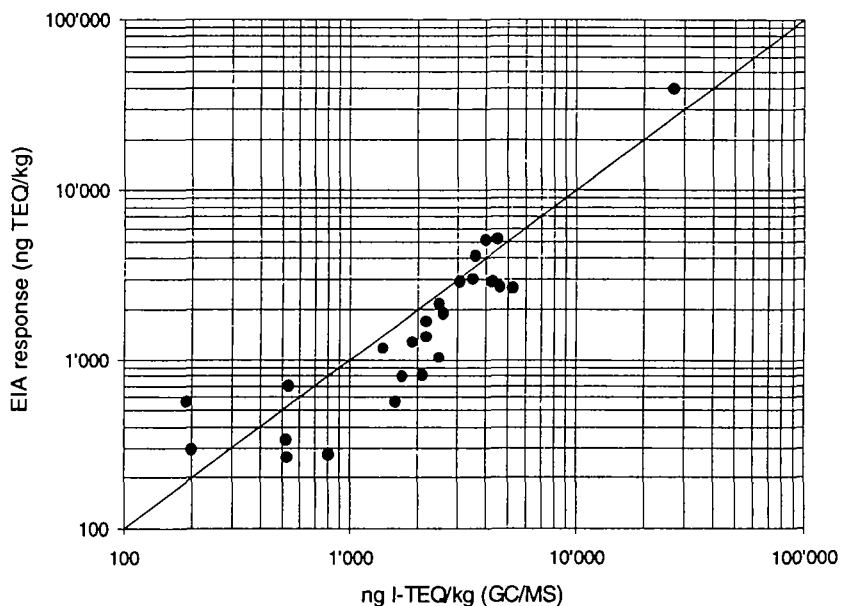


Figure 1: Comparison of TEQ determined by EIA and TEQ calculated by application of I-TEFs to single PCDD and PCDF congener concentrations from GC/MS analysis (bisector: EIA response = TEQ calculated from GC/MS data).

Figure 1 also shows that the sensitivity of the EIA covers the whole concentration range of the 25 samples. The specified sensitivity of the EIA used in this work is 19.5 ± 2.2 pg 2378-TCDD/tube (50 % inhibition).

The comparison confirms that this EIA is sufficiently reliable for the determination of TEQs of fly ash. As the EIA does not require any time consuming steps in the sample preparation (e.g. chromatographic methods) it is suitable as a simple and rapid screening method for large sample numbers in order to select critical samples for detailed investigation by GC/MS analysis.

Table 1: Comparison of EIA cross reactivities and I-TEFs [6] of the 2,3,7,8-chlorosubstituted PCDD and PCDF congeners and some other PCDDs and PCBs.

PCDDs	EIA cross reactivity	I-TEF	PCDFs	EIA cross reactivity	I-TEF
2378-TCDD	1	1	2378-TCDF	0.20	0.1
12378-PeCDD	1.05	0.5	12378-PeCDF	0.046	0.05
123478-HxCDD	0.016	0.1	23478-PeCDF	0.17	0.5
123678-HxCDD	0.079	0.1	123478-HxCDF	0.004	0.1
123789-HxCDD	0.39	0.1	123678-HxCDF	0.01	0.1
1234678-HpCDD	0.0072	0.01	123789-HxCDF	0.033	0.1
OCDD	< 0.00001	0.001	234678-HxCDF	0.049	0.1
			1234678-HpCDF	0.00022	0.01
			1234789-HpCDF	0.0094	0.01
			OCDF	< 0.00001	0.001
other PCDDs			PCBs		
23-DiCDD	0.003	-	PCB 77 ¹⁾	0.004	-
237-TriCDD	0.39	-	PCB 126 ²⁾	0.005	-
1234-TCDD	< 0.001	-	PCB 153 ³⁾	< 0.001	-
			PCB 169 ⁴⁾	< 0.001	-
			Aroclor 1254	< 0.001	-

¹⁾3,3',4,4'-Tetrachlorobiphenyl²⁾3,3',4,4',5-Pentachlorobiphenyl³⁾2,2',4,4',5,5'-Hexachlorobiphenyl⁴⁾3,3',4,4',5,5'-Hexachlorobiphenyl

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