ANALYSIS OF POLYHALOGENATED DIBENZOFURANS AND DIBENZO(P)DIOXINS (PXDF/Ds) IN THE SCOPE OF AN INTERLABORATORY TEST

W. Funcke, J. Mayer
GfA - Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH
D-48 161 Münster-Roxel, Otto-Hahn-Straße 22, Germany
M. Wilken
ITU - Ingenieurgemeinschaft Technischer Umweltschutz GmbH
D-10 829 Berlin, Kolonnenstraße 26, Germany

1. Introduction

A dust/soot sample was analyzed for polychlorinated dibenzofurans and dibenzo(p)dioxins (PCDF/Ds), polybrominated dibenzofurans and dibenzo(p)dioxins (PBDF/Ds) and mixed halogenated (bromine/chlorine) dibenzofurans and dibenzo(p)dioxins (PBCDF/Ds) by the laboratories of GfA and ITU in the scope of an interlaboratory test. While in the past a lot of interlaboratory tests have been realized with regard to the analysis of PCDF/Ds, the main objective of this work, which was performed with a view to emission measurements at a waste incineration plant, was the analysis of PBDF/Ds and PBCDF/Ds.

2. Methods

Each laboratory analyzed a part of the original solid sample as well as a part of the sample extract which was prepared by the other laboratory; each laboratory applied its own methods for extraction, clean-up and analysis of the PXDF/Ds. Partly, double and triple analyses were carried out. A general description of the methods is given as follows:

After soxhlet extraction of the solid sample with toluene the extract was divided into two portions; one portion was exchanged with the other laboratory. Each extraction portion was supplied with a mixture of ^{13}C-labeled PXDF/D quantification standards and cleaned-up in several steps. Finaly, further ^{13}C-labeled standards were added to the samples for determination of recovery rates of the first added quantification standards. The consecutive analyses were carried out by high resolution gas chromatography combined with high resolution as well as low resolution mass spectroscopy.

3. Results and Discussion

The results of the analyses are shown as total values and I-TEQ values in the figures 1 to 3. Although the sample treatment and analytical steps were not disputed between the laboratories prior to performing the analyses, the results for PCDF/Ds, PBDF/Ds and PBCDF/Ds of the two laboratories are in good accordance considering that the matrix was relatively difficult to analyze due to high carbon concentrations. As shown in figure 1 Tetra- to OctaCDF/Ds could be detected in all analyses. The I-TEQ values that are calculated to assess PCDF/D concentrations differ 15 % maximum from the mean value of all analyses performed. Also Tetra- to HexaBDF/Ds and partly HeptaBDF/Ds were detected and determined with good agreement betwen the two laboratories (fig 2).

Systematical differences between the results presented by the two laboratories can only be observed for PBCDF/Ds (fig 3). While PBCDDs could only be detected by ITU using high resolution mass spectroscopy, these compounds were not detected by GfA using low resolution mass spectroscopy. Within the PBCDFs GfA usually found higher concentration values than ITU. These differences are probably due to different clean-up procedures or to the quality of the ^{12}C standards. Additional tests should be done to find out the reasons for these differences.

As expected, the dispersion of individual results from multiple analyses performed by GfA increases from PCDF/Ds over PBDF/Ds to PBCDF/Ds. Qualitative differences between the extraction methods of the two laboratories cannot be determined.

4. Acknowlement

This work was sponsored by the Association of Plastics Manufakturers in Europe (APME) and the European Isocyanate Producers Association (ISOPA).

Fig. 1

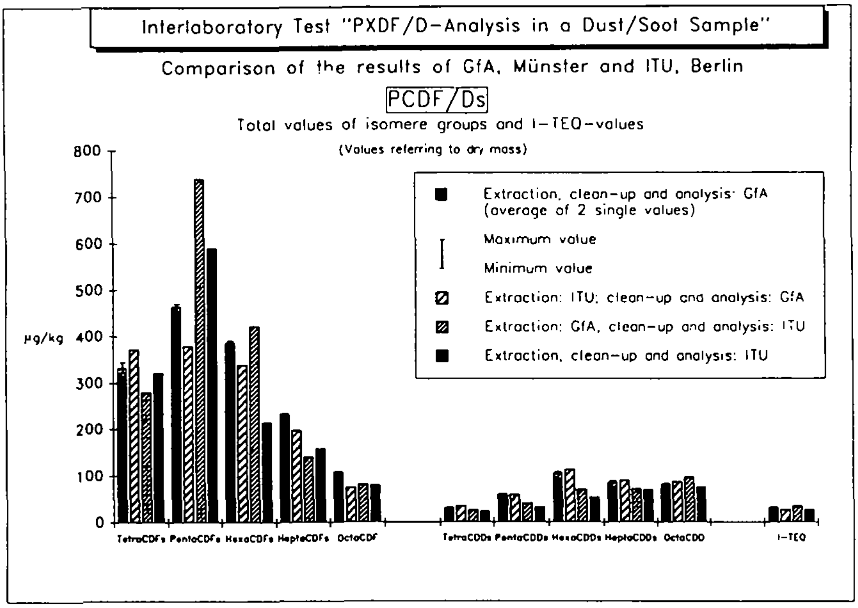

Interlaboratory Test "PXDF/D-Analysis in a Dust/Soot Sample"
Comparison of the results of GfA, Münster and ITU, Berlin
PCDF/Ds
Total values of isomere groups and I-TEQ-values
(Values referring to dry mass)
800
700
600
500
µg/kg 400
300
200
100
0
■ Extraction, clean-up and analysis: GfA (average of 2 single values)
Maximum value
Minimum value
▨ Extraction: ITU; clean-up and analysis: GfA
▨ Extraction: GfA, clean-up and analysis: ITU
■ Extraction, clean-up and analysis: ITU
TetraCDFs
PentaCDFs
HexaCDFs
HeptaCDFs
OctaCDF
TetraCDDs
PentaCDDs
HexaCDDs
HeptaCDDs
OctaCDD
I-TEQ

Fig. 2

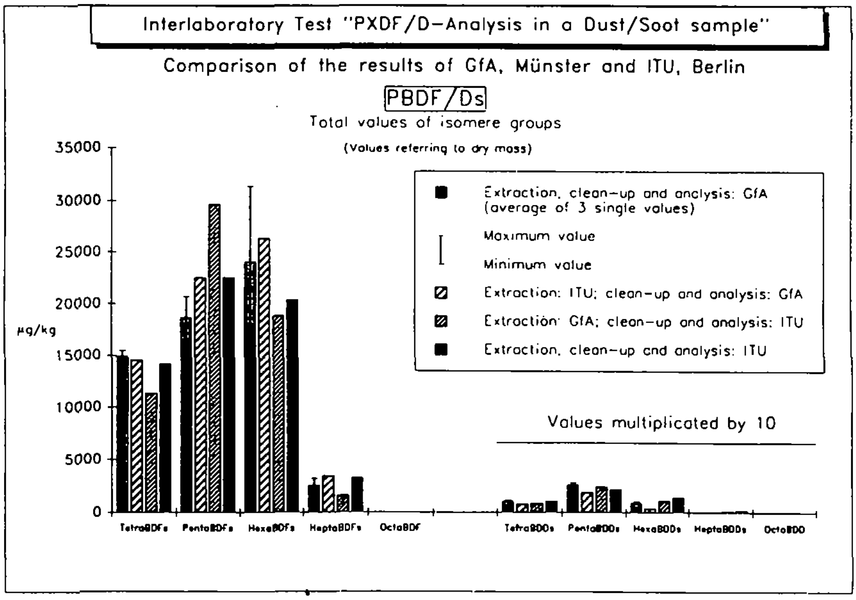
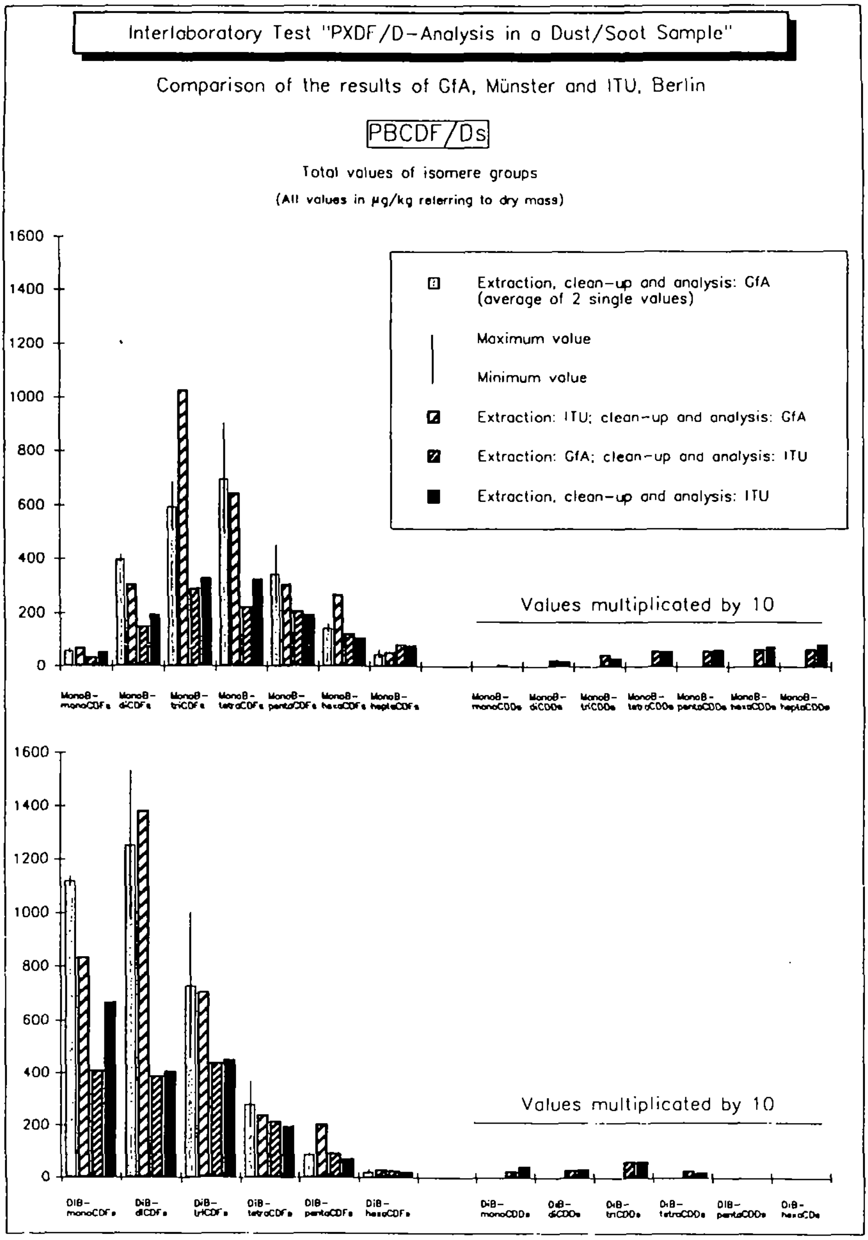

Interlaboratory Test "PXDF/D-Analysis in a Dust/Soot sample"
Comparison of the results of GfA, Münster and ITU, Berlin
PBDF/Ds
Total values of isomere groups
(Values referring to dry mass)
35000
30000
25000
20000
µg/kg
15000
10000
5000
0
■ Extraction, clean-up and analysis: GfA (average of 3 single values)
Maximum value
Minimum value
▨ Extraction: ITU; clean-up and analysis: GfA
▨ Extraction: GfA; clean-up and analysis: ITU
■ Extraction, clean-up and analysis: ITU
Values multiplicated by 10
TetraBDFs
PentaBDFs
HexaBDFs
HeptaBDFs
OctaBDF
TetraBDDs
PentaBDDs
HexaBDDs
HeptaBDDs
OctaBDD

Fig. 3


Interlaboratory Test "PXDF/D-Analysis in a Dust/Soot Sample"
Comparison of the results of GfA, Münster and ITU, Berlin
PBCDF/Ds
Total values of isomere groups
(All values in µg/kg referring to dry mass)
Extraction, clean-up and analysis: GfA (average of 2 single values)
Maximum value
Minimum value
Extraction: ITU; clean-up and analysis: GfA
Extraction: GfA; clean-up and analysis: ITU
Extraction, clean-up and analysis: ITU
Values multiplicated by 10
1600
1400
1200
1000
800
600
400
200
0
MonoB-monoCDFs
MonoB-diCDFs
MonoB-triCDFs
MonoB-tetraCDFs
MonoB-pentaCDFs
MonoB-hexaCDFs
MonoB-heptaCDFs
MonoB-monoCDDs
MonoB-diCDDs
MonoB-triCDDs
MonoB-tetraCDDs
MonoB-pentaCDDs
MonoB-hexaCDDs
MonoB-heptaCDDs
DiB-monoCDFs
DiB-diCDFs
DiB-triCDFs
DiB-tetraCDFs
DiB-pentaCDFs
DiB-hexaCDFs
DiB-monoCDDs
DiB-diCDDs
DiB-triCDDs
DiB-tetraCDDs
DiB-pentaCDDs
DiB-hexaCDs