

Dioxins and Furans

1. Background

The group of Polychlorinated Dibenzop-dioxins (PCDDs, Dioxins) and Polychlorinated Dibenzofurans (PCDFs, Furans), colloquially often referred to as “Dioxins” consists of 210 tricyclic chlorine organic compounds (congeners), that differ widely in the chlorine content and their respective toxicity. In particular 17 of the 210 compounds are extremely toxic. These congeners have a chlorine substitution in the 2,3,7,8-position. The most well-known compound is the 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) which is generally known as “Seveso Dioxin”. In February 1997 the World Health Organization (WHO) declared this substance as carcinogenic for humans.

Dioxins are mainly formed as unwanted by-product in combustion processes in case of which traces of chlorine are present. In former times waste incinerators and various industrial processes and productions have been the main source for dioxin contaminations, e.g. the chlorine-bleaching in the paper industry and the manufacture of certain chlorinated hydrocarbons (PCP, PCB, 2,4,5-Trichlorophenol). Due to technical improvements and legal stipulations dioxin emissions in Germany and thus, the contamination of the environment and humans has significantly decreased during the last years.

Dioxins and furans are extremely stable, both in terms of their chemical and thermal qualities. They have a very good liposolubility and are biologically nearly non-degradable (persistent). They are accumulated via the food chain and settle in the fat, liver and skin tissue of humans. The toxicity of dioxins and furans is calculated with the help of the toxicity equivalence factors scheme (TEF) specified by the World Health Organization (WHO). Added together they form the TEQ value (“Toxicity Equivalent”) which is reported.

Within the European Union a variety of legal regulations are in place that specify the limit and action values for dioxins; among others for waste incinerations, wastes in general, soil, sewage sludge, water and for the marketing and use of chemicals. Comprehensive legal regulations are also in place for feed and food.

Apart from the chlorinated PCDD/Fs, also the analogue brominated (PBDD/Fs) and mixed brominated/ chlorinated (“mixed halogenated”, “polyhalogenated”) dioxins and furans (PXDD/Fs, X = Br, Cl) are of environmental relevance.

2. Analysis parameters

Polychlorinated Dibenzodioxins and Furans (PCDD/Fs)

PCDDs	PCDFs
2,3,7,8-TetraCDD	2,3,7,8-TetraCDF
1,2,3,7,8-PentaCDD	1,2,3,7,8-PentaCDF
1,2,3,4,7,8-HexaCDD	2,3,4,7,8-PentaCDF
1,2,3,6,7,8-HexaCDD	1,2,3,4,7,8-HexaCDF
1,2,3,7,8,9-HexaCDD	1,2,3,6,7,8-HexaCDF
1,2,3,4,6,7,8-HeptaCDD	1,2,3,7,8,9-HexaCDF
OctaCDD	2,3,4,6,7,8-HexaCDF
	1,2,3,4,6,7,8-HeptaCDF
	1,2,3,4,7,8,9-HeptaCDF
	OctaCDF

The supplementary test of samples for group totals Tetra to HeptaCDD/F, Mono to TriCDD/F and non-2,3,7,8 substituted PCDD/F can be carried out on request.

Polybrominated Dibenzodioxins and Furans (PBDD/Fs)

PBDDs	PBDFs
2,3,7,8-TetraBDF	2,3,7,8-TetraBDD
1,2,3,7,8-PentaBDF	1,2,3,7,8-PentaBDD
2,3,4,7,8-PentaBDF	1,2,3,4,7,8-/1,2,3,6,7,8-HexaBDD
1,2,3,4,7,8-/1,2,3,6,7,8-HexaBDF	1,2,3,7,8,9-HexaBDD
1,2,3,4,6,7,8-HeptaBDF	OctaBDD
1,2,3,4,7,8,9-HeptaBDF	
OctaBDF	

The supplementary test of samples for group totals Tetra to HeptaBDD/F and Mono to TriBDD/F can be carried out on request.

Mixed Halogenated Dioxins and Furans (PXDD/Fs)

PBCDDs	PBCDFs
Total MonoBrDD	Total MonoBrDF
Total MonoBr-MonoCDD	Total MonoBr-MonoCDF
Total MonoBr-DiCDD	Total MonoBr-DiCDF
Total MonoBr-TriCDD	Total MonoBr-TriCDF
Total MonoBr-TetraCDD	Total MonoBr-TetraCDF
Total MonoBr-PentaCDD	Total MonoBr-PentaCDF
Total MonoBr-HexaCDD	Total MonoBr-HexaCDF
Total MonoBr-HeptaCDD	Total MonoBr-HeptaCDF
Total DiBrDD	Total DiBrDF
Total DiBr-MonoCDD	Total DiBr-MonoCDF
Total DiBr-DiCDD	Total DiBr-DiCDF
Total DiBr-TriCDD	Total DiBr-TriCDF
Total DiBr-TetraCDD	Total DiBr-TetraCDF
Total DiBr-PentaCDD	Total DiBr-PentaCDF
Total DiBr-HexaCDD	Total DiBr-HexaCDF
Total TriBrDD	Total TriBrDF
Total TriBr-MonoCDD	Total TriBr-MonoCDF
Total TriBr-DiCDD	Total TriBr-DiCDF

The analysis is usually carried out on a selection of PCDD/F, PBDD/F and PXDD/F compounds specified by the customer.

3. Testing methods

- The determination in sewage sludge and soil is made according to the German Sewage Sludge Ordinance (AbfKlärV).
- The determination in solid matters (soil, fire residues, wipe samples, waste, material samples) is made in accordance with DIN 38414-S24.
- The determination in food and feed complies with the requirements of the EC Regulations (Regulation (EU) No. 589/2014 and Regulation (EU) No. 709/2015 amending Regulation (EC) No. 152/2009) in respect of methods and quality.
- The determination in air, exhaust emissions, dusts, filter dust, ash, slag and soil is carried out analogous to E VDI 3499.
- The determination in emission samples is carried out in accordance with DIN EN 1948 and VDI 3499.
- The determination in ambient air and indoor air samples is made in acc. to VDI 3498 and VDI 2090.
- The determination in air samples as part of workplace measurements is carried out in accordance with measurement procedure for polychlorinated Dibenzofurans und Dibenzo-p-dioxins (IFA-Arbeitsmappe No.: 6880 "Messung von Gefahrstoffen")
- The determination in further matrices such as water, sludge, sediments, plants, compost, residual substances, substances for recycling, wood, textiles, cellulose products, mineral oils, chemicals, plastics, biota, animal and plant fats and oils is accredited according to DIN EN ISO/IEC 17025:2005.
- The determination in human samples (e.g. blood, breast milk) is accredited in accordance with DIN EN ISO/IEC 17025:2005.
- In the GMP laboratory the analyses for dioxins/furans, PCBs (dioxin-like and ICES-6) as well as polybrominated diphenyl ethers are made according to GMP quality standards (Good Manufacturing Practice), secured by governmental inspections acc. to § 64 German Pharmaceuticals Act.

The fundamental analysis steps for all matrices are as follows:

- Sample preparation
- Addition of all PCDD/F components to be determined as internal $^{13}\text{C}_{12}$ marked PCDD/F standard substances
- Extraction
- Clean-up of the extract by column chromatography
- Analysis by means of high resolution mass spectrometry (HRGC/HRMS) and GC/MS-Triple Quad
- Quantification of the native PCDD/Fs via the internal $^{13}\text{C}_{12}$ marked standards (isotope dilution method)

4. Quantification limits, sample quantities and sample transport

Matrix	Routine determination limit	Sample quantity	Preferred sample containers
Food	0,1 – 0,8 pg WHO-TEQ/g product or fat	300 g – 1000 g original sample, depending on fat content	amber glass vessel
Feed	0,08 – 0,9 ng WHO-TEQ/kg (related to 12 % humidity)	200 g original sample	amber glass vessel
Oils, fats	0,15 – 0,3 pg WHO-TEQ/g	50 g original sample	amber glass vessel
Biota	0,1 ng WHO-TEQ/kg dry mass	50 g dry mass	amber glass vessel
Food for babies and infants	0,02 pg WHO-TEQ/g ready to eat product	300 g – 1000 g original sample	amber glass vessel
Sludge, sediment, soil	1 ng WHO-TEQ/kg	100 g original sample	amber glass vessel
Sewage sludge	1,5 ng WHO-TEQ/kg	1000 g original sample	amber glass vessel
Waste, residues	0,001 µg WHO-TEQ/kg	200 g original sample	amber glass vessel
Ash, slag	0,001 µg WHO-TEQ/kg	200 g original sample	amber glass vessel
Exhaust gas	0,001 ng WHO-TEQ/m ³	10 m ³	XAD cartridge
Indoor air	0,2 pg WHO-TEQ/m ³	10 m ³	PU foam
Wipe samples	0,1 ng WHO-TEQ/m ²	0,1 m ²	amber glass vessel
Waste water	0,01 ng WHO-TEQ/l	2 x 1 l liquid	amber glass vessel
Water, drinking water	0,002 ng WHO-TEQ/l	4 x 1 l liquid	amber glass vessel
Commodities	depending on the matrix	after consultation	amber glass vessel
Materials, chemicals, polymers	depending on the matrix	after consultation	amber glass vessel
Human samples (e.g. blood)	depending on the matrix	after consultation	after prior consultation

After consultation additional matrices can also be analysed.

5. Licenses and quality assurance

Eurofins GfA Lab Service GmbH is accredited for determining dioxins (PCDD) and furans (PCDF) in accordance with DIN EN ISO/IEC 17025:2005.

Officially appointed measuring site in accordance with § 26 BImSchG (Federal Immission Control Act, parts M2, N2)

Testing centre for soil and sewage sludge according to § 3 AbfKlärV (German Sewage Sludge Ordinance)

Analytical services according to GMP guidelines (Good Manufacturing Practice), secured by governmental inspections acc. to § 64 German Pharmaceuticals Act

FDA registration of the GMP laboratory (U.S. Food and Drug Administration)

QS approved laboratory for feed monitoring

GOED member (Global Organization for EPA and DHA Omega-3)

Member of the International Fishmeal and Fish Oil Organization (IFFO)

Regular successful participation in following interlaboratory comparisons (extensive list available on request)

- FAPAS (Food Analysis Performance Assessment Scheme), Sand Hutton, York, UK
- QUASIMEME - Quality Assurance of Information for Marine Environmental Monitoring in Europe, Wageningen NL
- Folkehelseinstituttet, Norwegian Institute of Public Health, Oslo, Norway
- International Intercalibration Study – INTERCAL, Bert van Bavel, Dyltabruk, Sweden
- LUFA Speyer, 5-country interlaboratory trial on sewage sludge regulation, Germany
- CIND, Labservice Analytica Srl., Italy

More than 25 years experience in analysing dioxins and furans

6. References

Examination of more than 50 fish oil samples for PCDD/Fs, PCBs and further POPs on behalf of LYSI hf., Iceland (2011-2014)

Examination of 26 human samples (breast tumour, fat tissue) for PCDD/Fs and PCBs (12+7+PCB 209) on behalf of the National Taiwan University Hospital (2011-2013)

Examination of ca. 51 fish oil capsules and Omega-3 for PCDD/Fs and PCBs as well as PCB 209 (congeners) on behalf of the GOED – Global Organization for EPA and DHA Omega-3s, Salt Lake City, USA (2012, 2013)

Stand-by contract including express and routine examinations of 42 food samples for the Hesse state laboratory (Landesbetrieb Hessisches Landeslabor, LHL, 2011, 2012, 2013)

Examination of 48 food samples for PCDD/F and PCB on behalf of the regional authority in Gießen (2011, 2012, 2013)

Examination of 80 calf, beef and butter samples for PCDD/Fs and PCBs on behalf of the BAG (Swiss public health office, 2012)

Monitoring of about 70 food samples (e.g. herring, muscle with skin, vendace roe, salmon muscle, eel muscle, flounder muscle, rainbow trout, egg yolk, elk subcutaneous, butter, milk, fish meal, perch, fermented Baltic herring, saithe, mackerel, horse fat, pangasius (catfish), food supplement fish oil based) for PCDD/Fs and PCBs on behalf of the National Food Administration Sweden (2007, 2008;

ongoing projects with similar samples and of similar size in 2009, 2010, 2011 and 2012)

Monitoring of cow's milk samples for PCDD/Fs, WHO-PCBs PBDD/Fs and BFRs on behalf of the Environmental Protection Agency Ireland (2005, 2007 - 2012)

Examination of 14 fish oil samples for PCDD/Fs, PCBs, PBDEs, PAHs and OCPs on behalf of LYSI hf., Iceland (2012)

Analysis of 17 fish samples for PCDD/Fs and PCBs on behalf of the Landesfischereiverband Westfalen und Lippe e.V. (2011)

Examination of 24 soil samples for PCDD/Fs and PCBs on behalf of the State Agency for Nature, Environment and Consumer Protection (Landesamt für Natur, Umwelt und Verbraucherschutz – LANUV) NRW, 2011

Examination of about 130 eel muscle filet samples for PCDD/Fs, PCBs, PBDEs, OCPs, PFCs and mercury on behalf of the State Agency for Nature, Environment and Consumer Protection North Rhine-Westphalia (Landesamt für Natur, Umwelt und Verbraucherschutz – LANUV) NRW, 2011

Examination of more than 50 fish oil samples for PCDD/Fs, PCBs and further POPs on behalf of LYSI hf., Iceland (2011, 2012)

Monitoring of cow milk samples for PCDD/Fs, WHO-PCBs, PBDD/Fs and BFRs on behalf of the Environmental Protection Agency Ireland (2005, 2007 – 2012)

Examination of about 50 chemical samples per year from the chlorine chemistry for PCDD/Fs and PCBs on behalf of Solvay SA, Brussels (1999 – 2012)

Analysis of 64 oils and fats for PCDD/Fs and PCBs on behalf of the Swiss Federal Ministry of Health (Bundesgesundheitsamt BAG, 2010)

Examination of 83 human samples (blood) for PCDD/Fs and PCBs on behalf of the National Measurement Institute, Australia (2010)

Analysis of 49 human samples (blood) for PCDD/Fs on behalf of the Military Medical University, Vietnam (2010)

Analysis of 70 imported fish samples for PCDD/Fs and PCBs on behalf of the Swiss Federal Health Office (BAG, 2009)

Examination of about 180 human samples (blood) for PCDD/Fs and PCBs on behalf of the Istituto Superiore di Sanita, Italy (2009)

Examination of about 30 human samples (blood) for PBDEs, PCDD/Fs and PCBs on behalf of the state health office of the German Regional Council Stuttgart (2009)

Examination of organic trace contaminations in Hessian flowing waters, sewages and sewage sludges, HLUG, Umweltplanung, Arbeits- und Umweltschutz, 1994 – 2004, 2009, 2010

Monitoring of buffalo milk and soil samples for PCDD/Fs and WHO-PCBs on behalf of the government of the Italian province of Campania (2008 - 2010)

7. Publications

- Neugebauer, F., Schröter-Kermani, C., Pöpke, O., Stegemann, D., Steeg, W., Organohalogen Compounds 73, 1340 - 1343 (2011), Analytical experiences within the German Environmental Specimen Bank: Time trends of PCDD/F and dl-PCB in bream (*Abramis Brama*) caught in german rivers
- Schröter-Kermani, C., Rappolder, M., Neugebauer, F., Pöpke, O., Organohalogen Compounds 73, 1325 - 1328 (2011), PCDD/F, and dl-PCB in terrestrial ecosystems: Are there correlations of levels or patterns in soil and roe deer liver?
- Neugebauer, F., Pöpke, O., Opel, M., Arkudas, R., Organohalogen Compounds 73, 1223 - 1226 (2011), PCDD/F and dl-PCB analysis of chicken eggs and related samples: Experiences with dioxin analysis during a dioxin crisis
- Neugebauer, F., Pöpke, O., Petersen, M., Opel, M., Organohalogen Compounds 72, 1135 – 1138 (2010), 24 POPs - Comprehensive analysis of all Stockholm Convention and candidate POPs in cod liver and salmon
- Neugebauer, F., Esposito, M., Opel, M., Pöpke, O., Gallo P., Cavallo S., Colarusso G., Rosa D'A., Sarnelli P., Baldi L., Iovane G., Serpe L., Organohalogen Compounds 71, 1203 – 1208 (2009), The Italian Buffalo milk case – results and discussion of PCDD/F and dl-PCB analysis in milk, feedingstuff and soil samples from Campania, Italy
- Grümping, R., Petersen, M., Neugebauer, F., Opel, M., Organohalogen Compounds 70, 582 – 585 (2008), Levels of dioxins, PCBs, BFRs, PFCs and organotins in fishery products from Latvia
- Neugebauer, F., Opel, M., Grümping, R., Organohalogen Compounds 70, 879 – 882 (2008), The analysis of mineral feed for dioxins and dioxin-like PCBs – results and challenges
- Grümping, R., Opel, M., Petersen, M., Organohalogen Compounds 69, 912 – 915 (2007), Brominated dioxins and brominated flame retardants in Irish cow's milk