Fast and Flexible Automated Sample Extraction of PCDD/Fs and PCBs with *X-TRACTION® for Feed Samples*

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Content

1. Introduction

Persistent organic pollutants (POPs) are highly toxic and persistent substances, which accumulate in the environment and pose risks on health. Since 2001 they are regulated by the Stockholm Convention and monitored accordingly. By this, the analysis of POPs got increasingly important, leading to a huge growth in sample numbers and the need for standardized yet fast, automated and low-cost methods and instruments at the same time.

Additionally, today's laboratories require instruments, where global regulations and changing methods can be implemented easily into their own processes. The workflow to analyze POPs include extraction, clean-up, evaporation steps and the final analysis.

To complete our existing automated sample preparation portfolio, we have launched a new extraction system called X-Traction® by LCTech in 2021.

Pressurized Fluid Extraction (PFE) is a sample extraction method that employs liquid solvents at elevated temperatures and pressures to prepare samples for analysis. While commonly known extraction system are using high pressure (100 - 150 bar) for their process, our newly introduced extraction system works with low pressure (max. 17 bar; LPFE (Low Pressure Fluid Extraction). Working in low-pressure range is sufficient for an excellent extraction efficiency with decreased wear-and-tear of instrument parts, higher longevity and a safe handling. The ease of use is further increased by the unique extraction cell-cover-lid locking mechanism.

This system can be upgraded from 1 to 6 devices, which are able to operate either sequentially or in parallel, with a different protocol on each device.

The system features fast extraction times, easy handling, no cross-contamination and high reproducibility. It can be used for the extraction of Dioxin and PCBs acc. to US EPA method 3545A, extractions test for other POPs like PBDES, PCNs, PFOS etc. are ongoing.

In this application note the extraction for Dioxin and PCB in different feed samples will be described.

2. Material and Methods

- **X-TRACTION®, LCTech GmbH**
  - Extraction cell, 75 mL (nominal volume)
  - Glass fiber filter (37 mm diameter)
  - SST Frits
  - Result vials (60 mL; 250 mL)

- **DEXTech Pure or DEXTech Heat or DEXTech 16, LCTech GmbH**
  - Acidic silica gel column
  - Alumina column
  - Carbon column

- **D-EVA, Martin Christ enhanced by LCTech GmbH**
  - Centrifuge vials
  - Temperature sensor

- **DFS HRMS, Thermo Fisher Scientific**
  - SSL-injector, HT8-PCB, 60 m, 0.25 µm film, 0.25 mm ID, Trajan
  - PTV-injector, RTX-Dioxin2, 60 m, 0.25 µm film, 0.25 mm ID, Restek

- **Standard Solutions**
  - EPA1613-LCS, ISS and CSS, Wellington Laboratories
  - EPA1613-PAR/Stock, Wellington Laboratories
  - PCB-LCS-H, ISS-H and CSS-H, Wellington Laboratories
  - PCB-Stock-A20, Wellington Laboratories
  - EDF-5526, Recovery Standard, CIL
  - EDF-5525-100x Internal Standard, CIL

- **Solvents**
  - n-Hexane, picograde
  - Acetone, picograde
  - Toluene picograde
  - Dichloromethane, picograde

- **Drying Agent**
  - Sodium polyacrylate (Sigma Aldrich)

3.   Filling of Extraction Cell

1. First put in reusable FEP O-ring into both lids:

NOTE: Ensure that the FEP O-ring is stable within the lid and does not fall out.

2. Put on the frit (SST) onto one end of the extraction cell:

NOTE: Keep sealing surfaces clean! In case of dirt or grains, use a clean brush and remove dirt carefully before putting on the frit again.

3. Put on the lid (equipped with FEP O-ring):

NOTE: Ensure that the lid has a solid magnetic connection to the extraction cell. We recommend turning the lid until you feel the magnetic force between the lid and the extraction cell.

4. Turn around the extraction cell and place glass fibre filter (P/N 19281) on the upper end of the extraction cell.

5. Carefully push down the glass fibre filter to the bottom of the extraction cell. Please use the plunger (P/N 19343), for the exact placement of the filter.

NOTE: Ensure that the glass fibre filter is pushed down equally on each side and has full contact to the inner diameter of the extraction cell.

6. Fill your sample. A funnel or a weighing boat is recommended to ensure accurate filling of the cell.

NOTE: Keep sealing surfaces clean! In case of dirt or grains, use a clean brush and remove dirt carefully.

NOTE: To ensure the function of the X-TRACTION® system, it is mandatory to keep a minimum 2 cm air-gap between the upper end of the extraction cell and the upper end of the sample volume within the extraction cell. Please only use free-flowing, dry samples. If sample is wet or fluid, please use sodium polyacrylate until sample is free-flowing and dry. **Never use sodium sulfate as drying agent as it could lead to clogging of the capillaries!**

7. Put on the frit (SST) onto the upper end of the extraction cell.

NOTE: Keep sealing surfaces clean! In case of dirt or grains, use a clean brush and remove dirt carefully.

8. Put on the lid (equipped with FEP O-ring):

NOTE: Ensure that the lid has a solid magnetic connection to the extraction cell. We recommend turning the lid until you feel the magnetic force between the lid and the extraction cell.

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4. Extraction of PCDD/F and PCB in Feed Samples

4.1 Sample Preparation

Homogenized feed samples (5 – 20 g; particle size < 1 mm) have been mixed with drying agent (sodium poly-acrylate) before the extraction. The amount of the drying agent depends on the water content of the samples. The ratio between sample and drying agent was between 1:0.5 and 1:2. It is important to have a dry, free-flowing sample before the extraction. Do not use sodium sulfate as drying agent, as it may lead to clogging of the tubes!

If the sample is already dry, with a very small particles size, glass powder can be added to increase the accessibility of solvent to the matrix.

Fill your mixed sample into the extraction cell. Please keep in mind, that the extraction cell does not get filled completely. For further details, please refer to the manual.

4.2 Extraction Conditions

The extraction conditions for the feed samples are shown in the figure above. The parameters shown, are meant as a starting point for further method development, as results may vary depending on matrix composition. Changing the parameters, (increasing number of cycles, temperature and holding time) may lead to better extraction efficiency.

The extracted samples were further processed with a DEXTech Plus or Pure instrument, evaporated and analysed for PCDD/Fs and PCB by HR-GCMS.

4.3   Results for Feed Samples
Comparison of X-TRACTION®- and Soxhlet Extraction Efficiency

Figure 1 shows the WHO-PCDD/F-TEQ results of 4 independent QC-sample extractions (FMP-1 – FMP-4) in comparison to the result of the same QC-sample extracted with Soxhlet. The 4 QC-samples show very little variation among themselves (RSD 3,6 %) as well as in comparison to the Soxhlet extraction (RSD 5,5%). All results are well in between the 10 % deviation marked with the black lines within the figure.

Figure 1 WHO-PCDD/F-TEQ (2005)
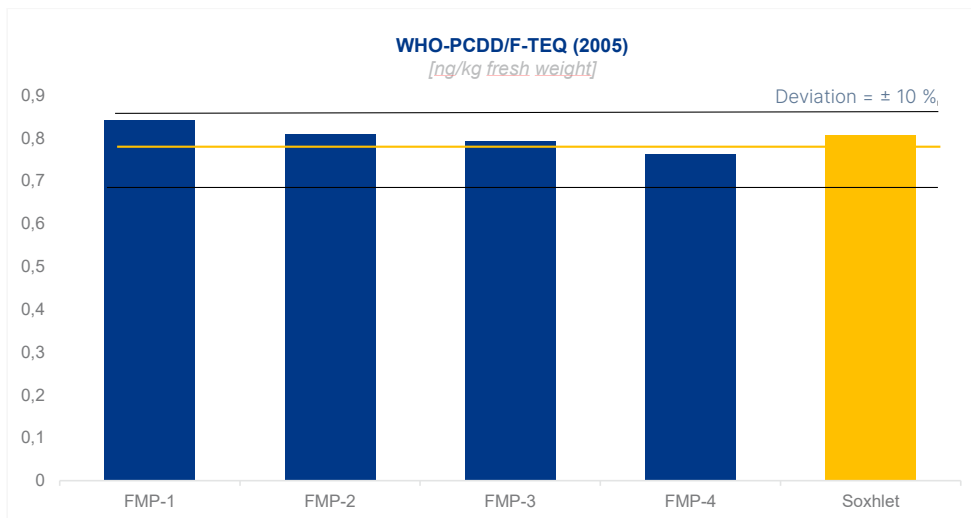
WHO-PCDD/F-TEQ (2005)
[ng/kg fresh weight]

Data provided by Chemical and Veterinary Analytical Institute, Münsterland-Emscher-Lippe (CVUA-MEL), Muenster, Germany

Figure 2 shows the SUM ndl-PCB results of the same samples described in figure 1. Also here you can see very little variation in the SUM ndl-PCB results (RSD 0,6%) among the 4 QC-samples as well as in comparison to the Soxhlet extraction (RSD 2,6%). Numerical data of the experiments is shown in the appendix.

Figure 2 SUM ndl-PCB

SUM ndl-PCB
[µg/kg fresh weight]

Data provided by Chemical and Veterinary Analytical Institute, Münsterland-Emscher-Lippe (CVUA-MEL), Muenster, Germany

As the results show, the efficiency and accuracy of X-TRACTION® extraction is comparable to classical Soxhlet extraction, but is much faster (45 minutes instead of several hours) and needs less solvent.

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4.4   Precision of X-TRACTION® Results

In Figure 3, 4 single extractions of the QC feed samples are compared. The results are shown for each PCDD/F and PCB congenere. Numerical data of the experiments is shown in the appendix.
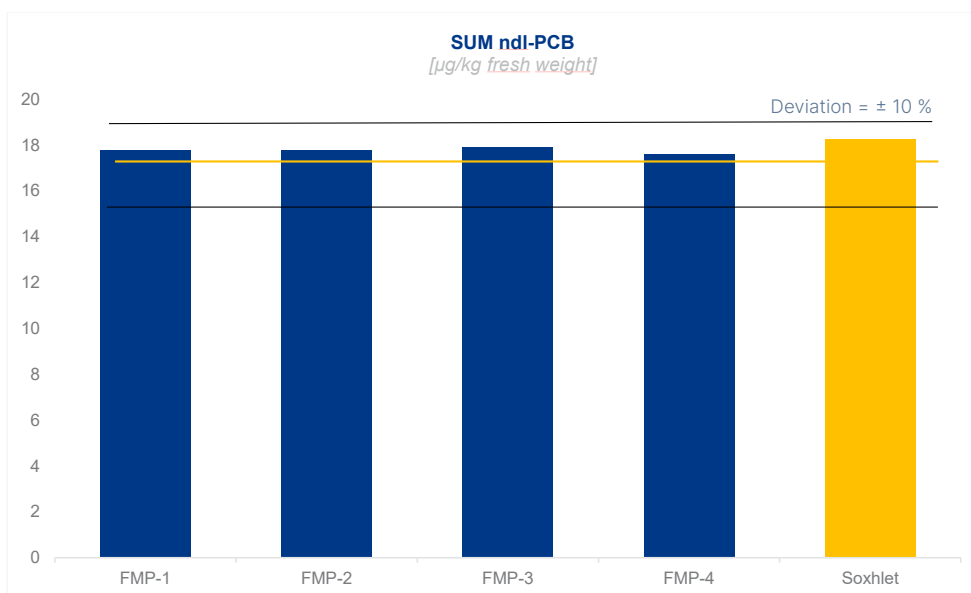
Figure 3 PCDD/F – 3 cycles

Data provided by Chemical and Veterinary Analytical Institute, Münsterland-Emscher-Lippe (CVUA-MEL), Muenster, Germany

Figure 4 PCB- 3 cycles
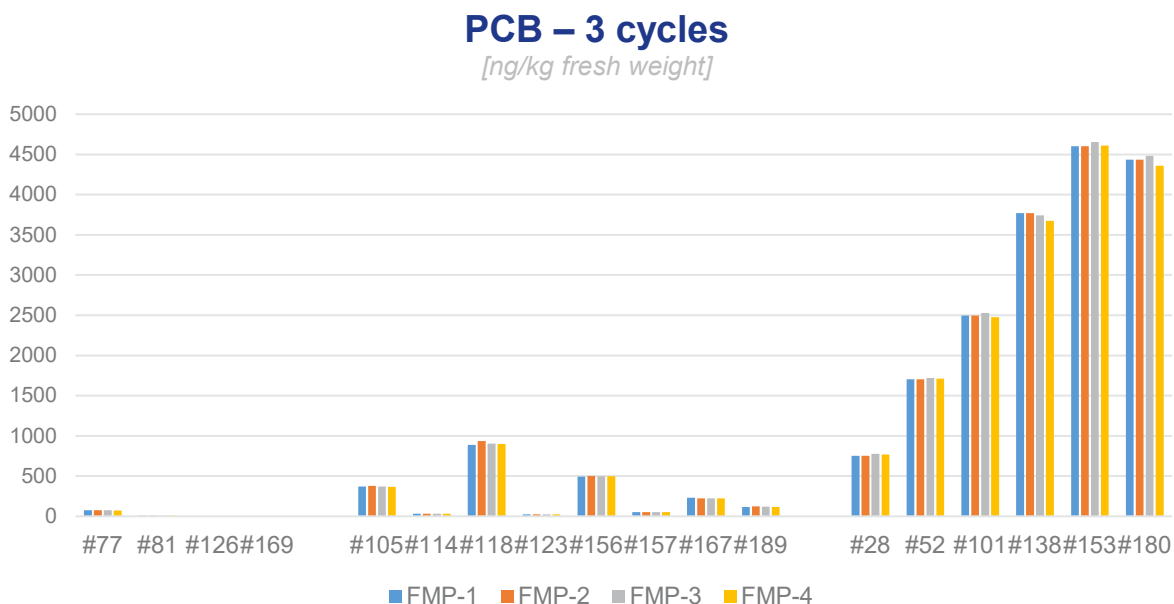
Data provided by Chemical and Veterinary Analytical Institute, Münsterland-Emscher-Lippe (CVUA-MEL), Muenster, Germany
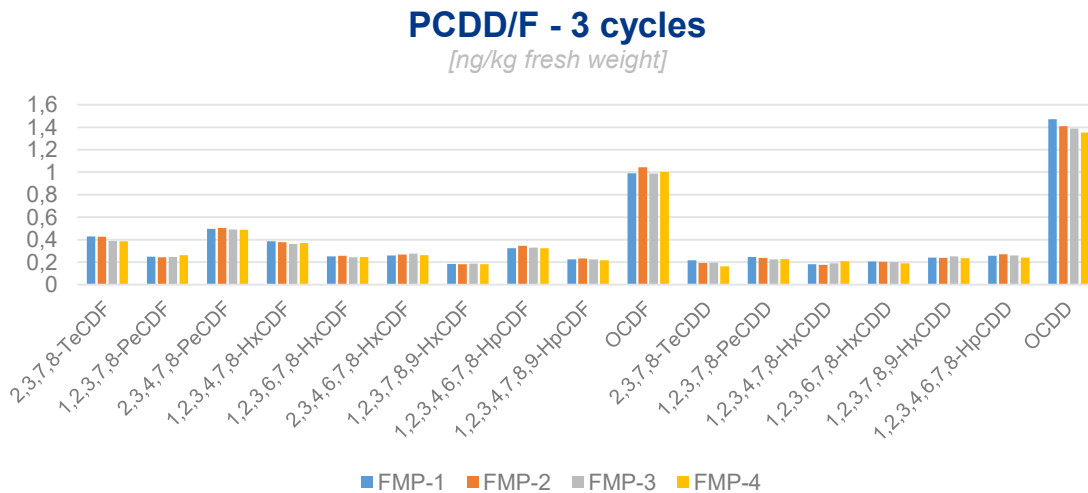
As the results show, the precision of the extraction with the X-TRACTION® system is very good with RSD values between 0.3 % and 9.8 % for the complete workflow (extraction, clean-up, evaporation and measurement).

5.   Conclusion

In summary, the results shown above proof that the X-TRACTION® system is a very flexible and reliable system for a variety of different samples (food, feed, environmental). The results show overall good precision and accuracy for the whole PCB and PCDD/F workflow, including extraction, clean-up, evaporation and analysis.

The handling of the X-TRACTION® system is very easy, fast and intuitive. Especially in comparison to classical extraction methods like Soxhlet, the system offers short extraction times and low solvent consumption.

6.   Acknowledgements

7. Appendix

Dioxin Workflow → From *Sample* to *Chromatography*

2 X-TRACTION®
For extraction

3 D-EVA Concentration
For the sensor controlled evaporation of extracts

4 DEXTech Product Family
Sample preparation for all types of PCB and dioxin analysis

DEXTech Columns
Universal and SMART

5 D-EVA Concentration
For the sensor controlled evaporation to a few µL

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1 Sample Preparation

- Sample intake / weigh in 5 to 10 g
- Homogenization with PAA / Hydromatrix
- Transfer into the extraction cell

2 Extraction: X-TRACTION®

- Sample intake
- Each cycle 20 min inclusive selfcleaning
- Up to 6 modules/extractions in parallel

Collection in

- 60 mL, 120 mL – bottle
- 140 mL – Centrifuge tubes for D-EVA (max. 90 mL capacity)

3 Evaporation: D-EVA

- Up to 11 × 90 mL in parallel without supervision
- Final volume approx. 1 mL
- n-hexane within approx. 40 min
- Toluene within approx. 60 min
- Manual transfer without rinsing to 15 mL Vials
- Add clean-up standard solution (n-Hex/Tol)
- Fill up to approx. 10 mL with n-hexane

4 Clean-up: DEXTech Pure / Plus and 16

- Fraction 1 in 40 mL centrifuge tubes containing PCB in 24 mL n-hexane/DCM
- Fraction 2 in 15 mL centrifuge tubes containing PCDD/F in 10 mL toluene

5 Evaporation: D-EVA

- Up to 23 x PCB or 26 x PCDD/F in parallel without supervision
- PCB within approx. 30 min to approx. 200-300 µL
- PCDD/F within approx. 40 min to 30-100 µL
- Manual transfer without rinsing to GC Vials with Insert
- Blowing down with nitrogen if necessary
- Add syringe standard solution

6 Ready for Analysis

- 6 samples in parallel
- within 5 hours
- manual handling approx. 15 min

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Table 1 Comparison X-TRACTION®/Soxhlet - feed samples

	X-TRACTION®							Soxhlet		
	FMP-1	FMP-2	FMP-3	FMP-4	Mean	Deviation	RSD %	Mean	Deviation	RSD%
	3 Cycles	3 Cycles	3 Cycles	3 Cycles	n = 4			n = 9		
	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg			Fresh weight ng/kg		
(WHO PCDD/F-TEQ 2005) upper bound	0.8429	0.8101	0.7943	0.7622	0.8024	0.0291	3.6	0.8070	0.0443	5.49
(WHO dl-PCB-TEQ 2005) upper bound	0.6081	0.6173	0.6095	0.591	0.6065	0.0096	1.6	0.6660	0.0243	3.65
(WHO-PCDD/F-PCB-TEQ 2005) upper bound	1.451	1.4274	1.4038	1.3532	1.4274	0.0193	1.3	1.4730	0.0401	2.72
Sum ndl-PCB upper bound	17.765	17.765	17.903	17.606	17.7598	0.1051	0.6	18.270	0.4682	2.56

Data provided by Chemical and Veterinary Analytical Institute, Münsterland-Emscher-Lippe (CVUA-MEL), Muenster, Germany

Table 2 Precision PCDD/F extraction - feed samples

	Extraction 1	Extraction 2	Extraction 3	Extraction 4	Mean	Deviation	RSD %
	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg		
Polychlorinated Dibenzofurane							
2,3,7,8-TeCDF	0.4292	0.4263	0.3877	0.3862	**0.4074**	**0.0204**	**5.0**
1,2,3,7,8-PeCDF	0.2477	0.2428	0.2462	0.2615	**0.2496**	**0.0071**	**2.9**
2,3,4,7,8-PeCDF	0.4973	0.5043	0.4909	0.4892	**0.4954**	**0.0059**	**1.2**
1,2,3,4,7,8-HxCDF	0.3864	0.3791	0.3631	0.3696	**0.3746**	**0.0089**	**2.4**
1,2,3,6,7,8-HxCDF	0.2518	0.256	0.2447	0.247	**0.2499**	**0.0044**	**1.7**
2,3,4,6,7,8-HxCDF	0.2585	0.2687	0.2752	0.2619	**0.2661**	**0.0064**	**2.4**
1,2,3,7,8,9-HxCDF	0.1844	0.1819	0.1881	0.1832	**0.1844**	**0.0023**	**1.3**
1,2,3,4,6,7,8-HpCDF	0.3229	0.3448	0.3284	0.3236	**0.3299**	**0.0088**	**2.7**
1,2,3,4,7,8,9-HpCDF	0.2241	0.2323	0.2236	0.2165	**0.2241**	**0.0056**	**2.5**
OCDF Octachlordibenzofuran	0.9901	1.043	0.9885	1.001	**1.0057**	**0.0221**	**2.2**
Polychlorinated Dibenzodioxin							
2,3,7,8-TeCDD	0.2163	0.1917	0.1949	0.1634	**0.1916**	**0.0188**	**9.8**
1,2,3,7,8-PeCDD	0.247	0.2377	0.2255	0.2275	**0.2344**	**0.0086**	**3.7**
1,2,3,4,7,8-HxCDD	0.1831	0.1759	0.19	0.2084	**0.1894**	**0.0121**	**6.4**
1,2,3,6,7,8-HxCDD	0.2067	0.2032	0.2019	0.1904	**0.2006**	**0.0061**	**3.1**
1,2,3,7,8,9-HxCDD	0.2422	0.2373	0.2526	0.2351	**0.2418**	**0.0067**	**2.8**
1,2,3,4,6,7,8-HpCDD	0.2567	0.2704	0.2598	0.2401	**0.2568**	**0.0109**	**4.2**
OCDD Octachlordibenzodioxin	1.472	1.409	1.389	1.353	**1.4058**	**0.0432**	**3.1**

Table 3 Precision PCB extraction - feed samples

	Extraction 1	Extraction 2	Extraction 3	Extraction 4	Mean	STABWN	RSD %
	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg	Fresh weight ng/kg		
non-ortho PCB							
PCB 77	74.58	77.17	77.39	73.8	**75.74**	**1.57**	**2.1**
PCB 81	6.957	7.275	6.708	6.934	**6.969**	**0.2019**	**2.9**
PCB 126	4.561	4.628	4.575	4.43	**4.549**	**0.0728**	**1.6**
PCB 169	2.542	2.546	2.516	2.405	**2.5023**	**0.0573**	**2.3**
mono-ortho PCB							
PCB 105	370.4	378.8	370.9	368.1	**372.1**	**4.0376**	**1.1**
PCB 114	33.57	33.36	33.13	31.39	**32.9**	**0.8643**	**2.6**
PCB 118	886.1	934.4	905.6	899.5	**906.4**	**17.64**	**1.9**
PCB 123	23.05	23.69	23.32	23.00	**23.3**	**0.2739**	**1.2**
PCB 156	493.1	503.8	496.7	498.8	**498.1**	**3.8710**	**0.8**
PCB 157	53.14	53.23	52.49	51.88	**52.7**	**0.5455**	**1.0**
PCB 167	229.7	224.5	224.4	223.6	**225.6**	**2.4213**	**1.1**
PCB 189	117.2	122.3	118.3	116.9	**118.7**	**2.1568**	**1.8**
ndl-PCB	µg/kg	µg/kg	µg/kg	µg/kg	**µg/kg**	**µg/kg**	
PCB 28	0.7508	0.7508	0.7764	0.7697	**0.7619**	**0.0114**	**1.5**
PCB 52	1.705	1.705	1.719	1.713	**1.7105**	**0.0059**	**0.3**
PCB 101	2.498	2.498	2.53	2.477	**2.5008**	**0.0189**	**0.8**
PCB 138	3.771	3.771	3.742	3.674	**3.7395**	**0.0396**	**1.1**
PCB 153	4.603	4.603	4.653	4.611	**4.6175**	**0.0208**	**0.4**
PCB 180	4.437	4.437	4.483	4.361	**4.4295**	**0.0438**	**1.0**

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8. Ordering information

- **X-TRACTION® MAIN SYSTEM**   P/N   20000

- **X-TRACTION® ADD-ON-SYSTEM**   P/N   20001

- **EXTRACTION CELL**   P/N   19700

- **RACK FOR EXTRACTION CELL**   P/N   19341

- **FLASS FIBER FILTER (100 PCS./PCK.)**   P/N   19281

- **PLUNGER FOR FILTER PLACEMENT**   P/N   19343

For a detailed quotation and more information about D-EVA and DEXTech products please contact LCTech.

9. Related Information and References

1. Bernsmann, T., Albrecht M., Fürst, P. (2016); Organohalogen Compounds Vol. 78, 797-799

2. Calaprice C, Calvano CD, Zambonin C, Focant JF (2015); Organohalogen Compounds Vol. 77, 733-735

3. Bernsmann, T., Albrecht M., Fürst, P. (2014); Organohalogen Compounds Vol. 76, 1281-1284

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