SOLUTIONS BY LCTech

Fast and Flexible Automated Sample Clean-up of PCDD/Fs and PCBs with DEXTech Systems

Content

1. Introduction

An increasing number of samples for PCDD/F and PCB analysis in recent year as well as major contamination cases have illustrated the need for high throughput methods to identify non-compliant samples. To meet the challenges of modern PCDD/F and PCB analysis and to react to an unexpected increase in sample load numbers, automated clean-up systems should be cost effective, fast and flexible in the fractionation of PCDD/Fs, and PCBs. Depending on the demands of the chosen analytical method (GC-MS/MS, HR-MS) and preferences of different routine labs a flexible fractionations of the target substances is desirable.

Automated clean-up systems often have only a limited flexibility regarding the fractioning of PCDD/Fs and PCBs. In many cases they separate two fractions with PCDD/F und non-ortho PCBs in one fraction and mono-ortho PCBs and ndl-PCBs in another fraction. Additionally, to the previously mentioned fractionations of the DEXTech Plus system (1, 2, 3) the DEXTech Pure system was developed to have additional, more flexible fractionation and clean-up possibilities.

2. Material and Methods

In order to compare the different possible methods of a DEXTech Pure/Heat system (LCTech GmbH), different oil samples were spiked with ^{13}C- standards, processed with a DEXTech Pure/Heat or DEXTech 16 sytem and revoeries of the ^{13}C- standards compared.

- 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
  - Toluene picograde
  - Dichloromethane picograde

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

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

  - Alumina column
  - Carbon column

- eVol RT, SGE electronic syringe
- DFS HRMS, Thermo Fisher Scientific
  - SSL-injector, HT8-PCB, 60m, 0.25 µm film, 0,25 mm ID, Trajan
  - PTV-injector, RTX-Dioxin2, 60m, 0.25 µm film, 0,25 mm ID, Restek

2.1 Sample Preparation

Sample composition and sample volume depends on the used columns and sample loop size.

Two different sample loops are available:

- The standard 15 mL sample loop with a max. sample volume of 12 mL
- 20 mL sample loop (P/N 15710) with a max. sample volume of 17 mL

In addition, LCTech provides different columns for the DEXTech Pure system depending on the individual requirements, matrix or the desired method.

1. Acidic silica column; depending on the fat content (Universal, SMART) – column 1
2. Alumina column 2
3. Carbon column; reusable – column 3

Figure 1: Universal, SMART, Alumina, and Carbon column as well as adapter for easy change between Universal and SMART column

Maximum fat capacity for Universal, and Standard column:	5 g
Maximum fat capacity for SMART column:	1.5 g

For the various oil samples in the tests, 3 g of the oil were mixed with 1 mL of toluene, spiked with the ^{13}C- standards and filled up to a final volume of 17 mL with n-hexane. Other solvents like methanol or acetone are tolerated to a maximum volume of 1 mL in a 17 mL sample.

The different samples were cleaned-up using one of the different methods:

- Alox Plus Method
- Alox Pure Method

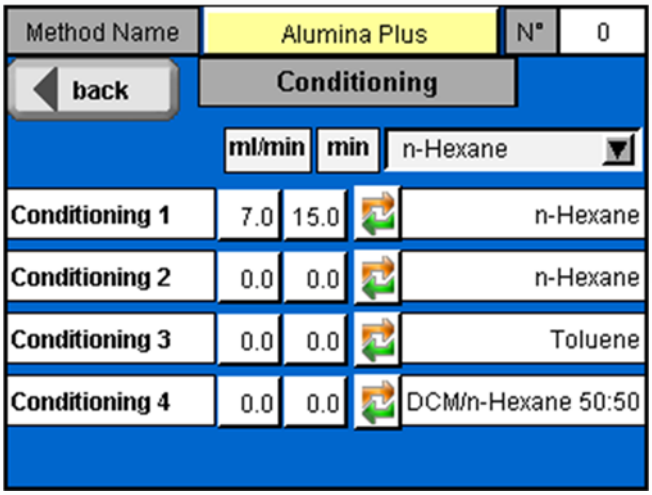
For samples where you are only intrested in dioxin or a PCB clean-up, the DEXTech Pure/Heat instrument also offers you the possibility of a cost effective 2 column method:

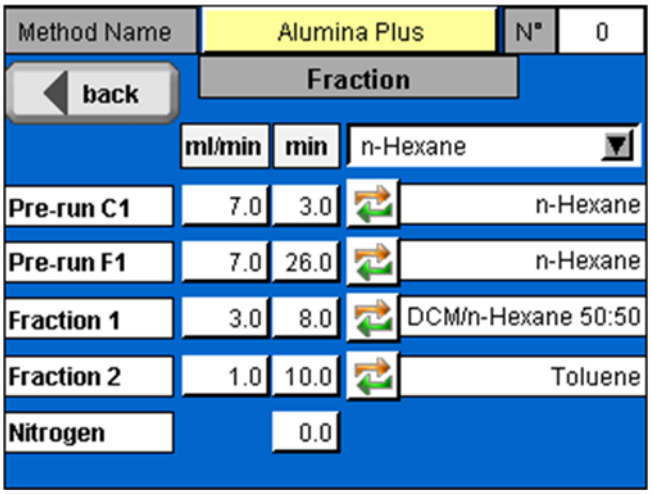
- Dioxin only Method
- PCB only Method

2.2 DEXTech Method Parameters

Alox Plus Method

Default method using the **Universal** column (column 1) together with the **Alumina** column (column 2) and a **Carbon** column (column 3).



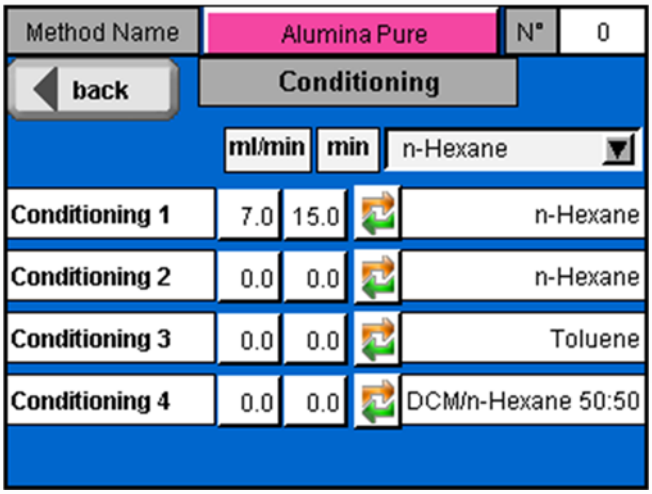


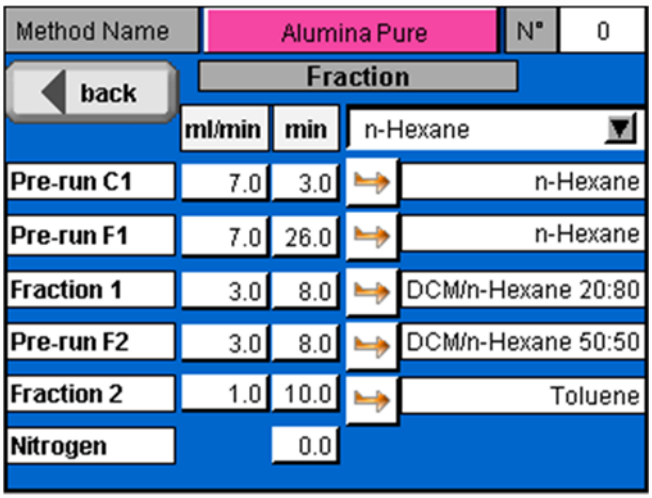
Fractioning:

Fraction 1: ndl-PCBs, mono-ortho-PCBs, PBDEs
Fraction 2: non-orthos-PCBs, PCDD/Fs

Alox Pure Method

Default method using the **Universal** column (column 1) together with the **Alumina** column (column 2) and a **Carbon** column (column 3).



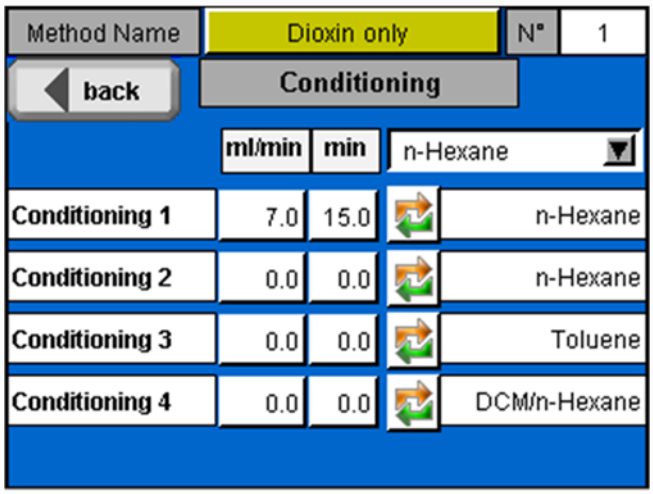


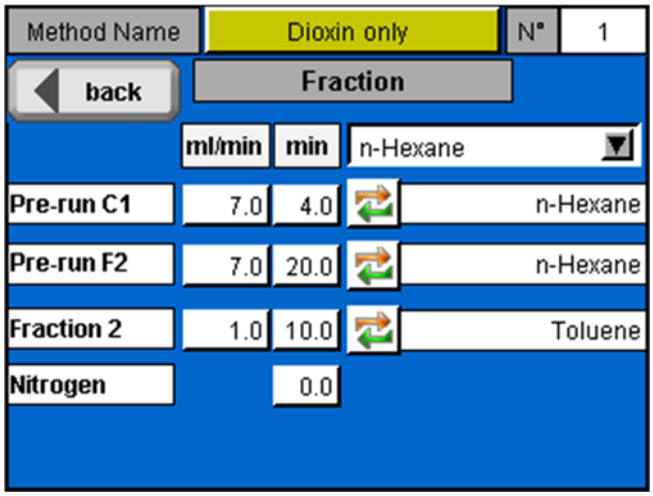
Fractioning:

Fraction 1: non-orthos-PCBs, ndl-PCBs, mono-ortho-PCBs, PBDEs
Fraction 2: PCDD/Fs

Dioxin only Method

Default method using the **Universal** column (column 1) and a **Carbon** column (column 3). **The Dummy column has to be placed on position 2.**



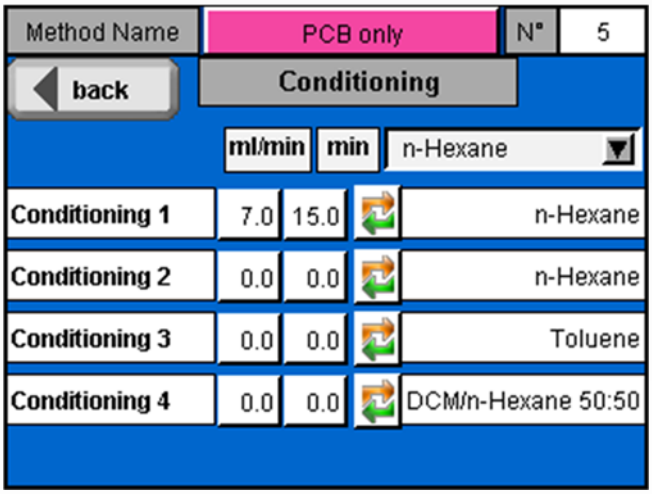


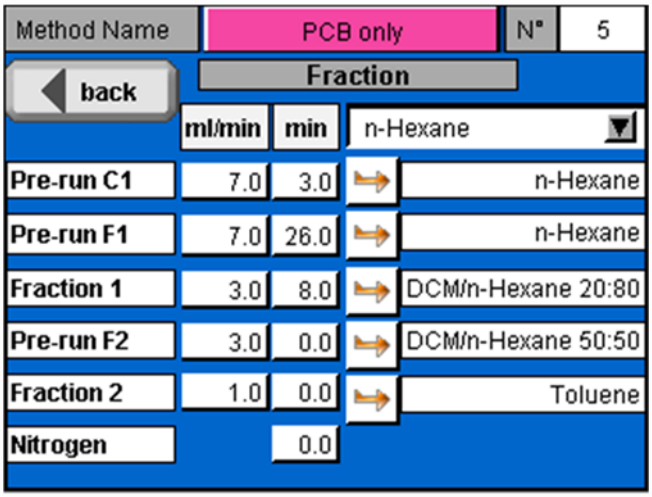
Fractioning:

Fraction 1: -
Fraction 2: PCDD/Fs

PCB only Method

Default method using the **Universal** column (column 1) and a **Alumina** column (column 2). **The Dummy column has to be placed on position 3.**





Fractioning:

Fraction 1: non-orthos-PCBs, ndl-PCBs, mono-ortho-PCBs, PBDEs

2.2.1 Sample Evaporation

After clean-up, the samples were evaporated down using the D-EVA vacuum centrifuge system.

Using D-EVA, a simultaneous sensor controlled evaporation of up to 26 samples for the 10 ml PCDD/F-Fraction (F2) with a final volume of 30 to 100 µL or up to 23 samples for the PCB-Fraction (F1) with a final volume of 300 to 500 µL is possible. The centrifuge chamber is heated via infrared light using halogen lamps free from UV wavelengths and even a pressure of down to 10 mbar is possible.

Due to the sensor in the D-EVA the standard program installed on the D-EVA will stop the evaporation at a point with a final volume of 100 – 200 µL for PCDD/F and 300 – 500 µL for PCB. Blowing down this final volume in the centrifuge tubes within a few minutes with N2 to nearly dryness is possible without any rinsing steps. Just transfer the sample with the recovery standard solution into the GC-vial.

2.3 Sample Measurement

All samples, kept in nonan, solvent blanks as well as the various oils were analysed with a DFS HRMS from Thermo Fisher Scientific.

2 µL of fraction 1 are injected splitless via SSL-injector (270 °C) onto a 60m HT8 PCB capillary column from Trajan (0.25 µm film thickness, 0,25 mm ID). The GC temperature starts with 140 °C rising up to 320 °C within 38 min. Helium as carriergas has a flow of 1.2 mL/min.

5 µL of fraction 2 is injected at 140 °C (after 2 min rising up to 320 °C) via PTV onto a 60m RTXDioxin2 capillary column from Resteck. (0.25 µm film thickness, 0.25 mm ID). The GC temperature starts with 140 °C rising up to 320 °C within 45 min. Helium as carriergas has a flow of 1.2 mL/min.

The HRMS Resolution has to be at minimum 10000. Reference gas is perflourphenantrene (FC5311).

3. Results

Using different combinations of the classical acidic silica, alumina and carbon clean-up, the DEXTech Pure system with its flexible fluidic system is able to clean-up and separate the PCDD/F, PCBs and PBDEs in a variety of fractions. Here the different available methods are shown with the corresponding flow path.

3.1 Method 1: 3-Column Clean-up DEXTech Plus Method

Fraction 1: ndl-PCBs, mono-ortho-PCBs

Fraction 2: non-ortho-PCBs, PCDD/F

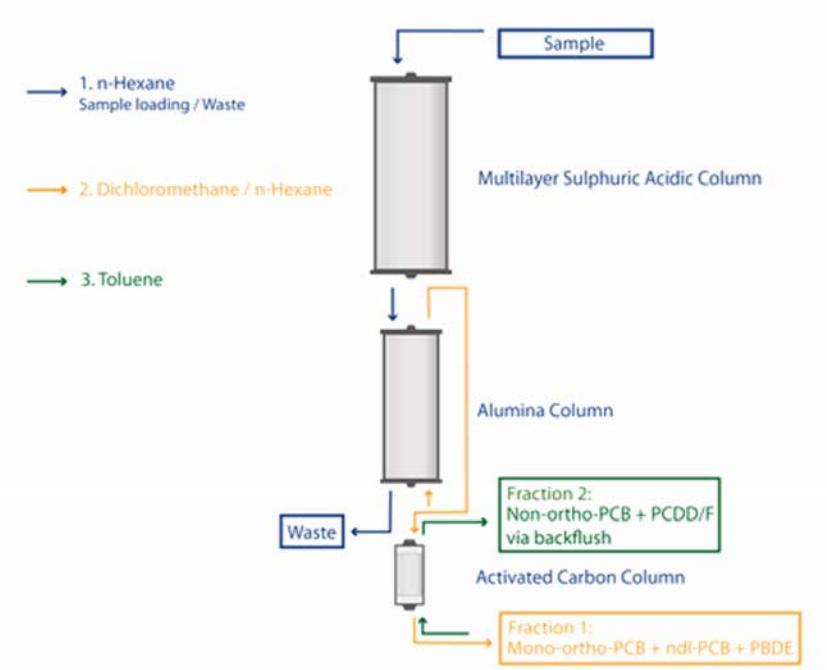


Figure 2: Flow Scheme – Alumina- Oxide Column (Alox Plus Method)

Using this method, the samples are cleaned-up with an acidic silica-, an alumina- and a carbon-column. There are two kinds of acidic silica-columns available. The Universal-column is used for fat samples with a maximum amount of fat of 5 g. The SMART-column is used for fat samples with a maximum amount of 1.5 g fat. Depending on the used acidic silica-column different process times and total solvent consumptions are possible. Table 1 summarizes the process times, solvent consumptions and fraction volumes for the different available methods on the DEXTech Pure system.

In this method, the sample is loaded in n-hexane over the acidic silica column onto the alumina column. The mono-ortho-PCBs and ndl-PCBs, the non-ortho-PCBs and the PCDD/Fs are flushed from the alumina-column by a mixture of n-hexane and dichloromethane (50:50 %) onto the carbon-column. While the mono-ortho-PCBs and ndl-PCBs are collected as Fraction 1, the non-ortho-PCBs and the PCDD/Fs are retained on top of the carbon-column. They are collected in an elution step with toluene as Fraction 2.

3.2 Method 2: 3-Column Clean-up DEXTech Pure Method

Fraction 1: ndl-PCBs, mono-ortho-PCBs, non-ortho-PCBs, PBDEs

Fraction 2: PCDD/Fs

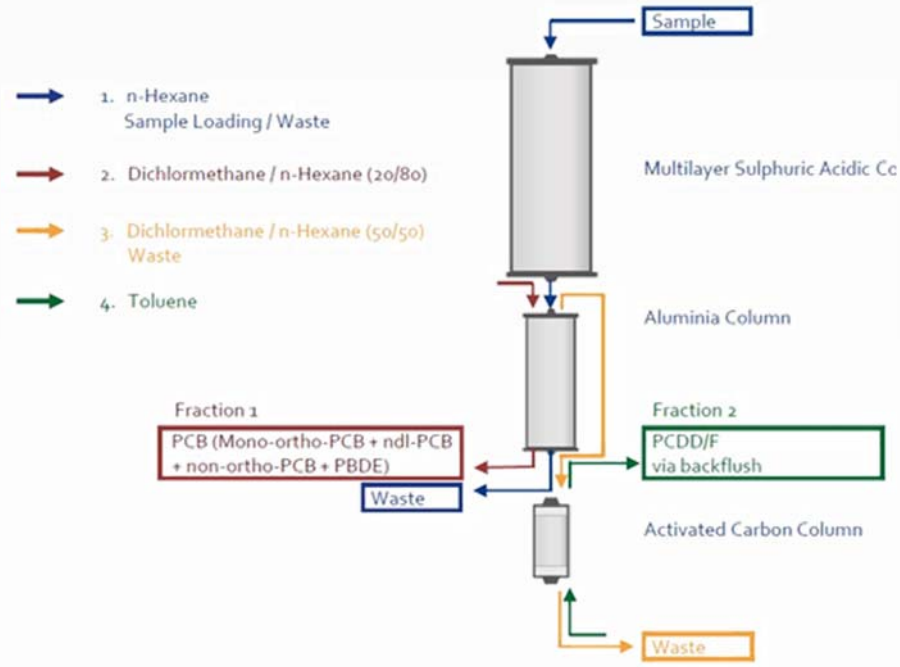


Figure 3: Flow scheme – Aluminium-oxide column (Alox Pure method)

Using this method, the samples are cleaned-up with an acidic silica-column, an alumina-column and a carbon-column also. Again, the samples are loaded in n-hexane over an acidic silica-column onto an alumina-column.

With a mixture of n-hexane and dichloromethane (80/20 %) the mono-ortho-PCBs and ndl-PCBs and non-ortho-PCBs are separated from the PCDD/Fs and are collected as Fraction 1. Afterwards, the PCDD/Fs are flushed from the alumina-column by a mixture of n-hexane and dichloromethane (50:50 %) onto the carbon-column. In a final step the PCDD/Fs are eluted with toluene from the carbon-column as Fraction 2.

3.3 Method 3: 2-Column Clean-up PCB only

Fraction 1: ndl-PCBs, mono-ortho-PCBs, non-ortho-PCBs, PBDEs

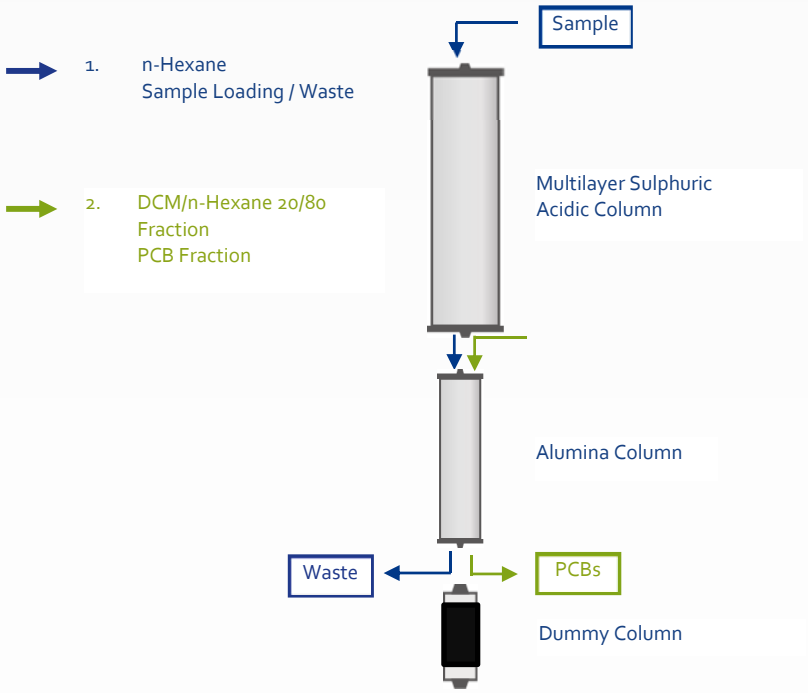


Figure 4: Flow Scheme – 2 Column "PCB Only"

For samples were no separation of the PCBs from the PCDDF/F is necessary and no PCDD/F fraction has to be collected, the 2-column PCB only method can be used. In this method, only the acidic silica-column and the alumina-column are used making it faster and more cost effective.

This method includes the same steps as method 2 (DEXTech Pure method) but it does not include the final separation steps with the elution of the PCDD/Fs from the alumina- and carbon-column.

3.4 Method 4: 2-Column Clean-up Dioxin only

Fraction 1: PCDD/Fs

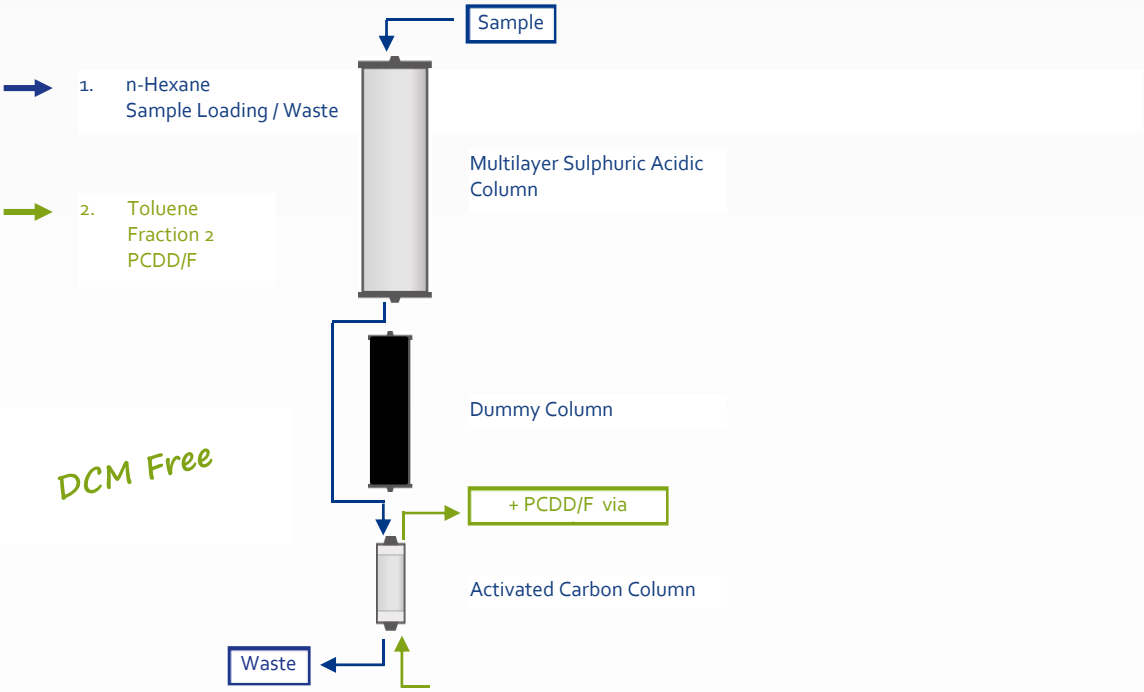


Figure 5: Flow Scheme – 2 Column "Dioxin Only"

Finally, a 2-column Dioxin only method has been developed and implemented on the DEXTech Pure system for sample were no PCB fraction is needed. In this method, the sample is loaded in n-hexane over the acidic-silica column directly onto the carbon-column.

Degradation products go to the waste while the PCDD/Fs will be trapped on the carbon-column. In a next step, the PCDD/Fs are collected from the carbon-column with toluene.

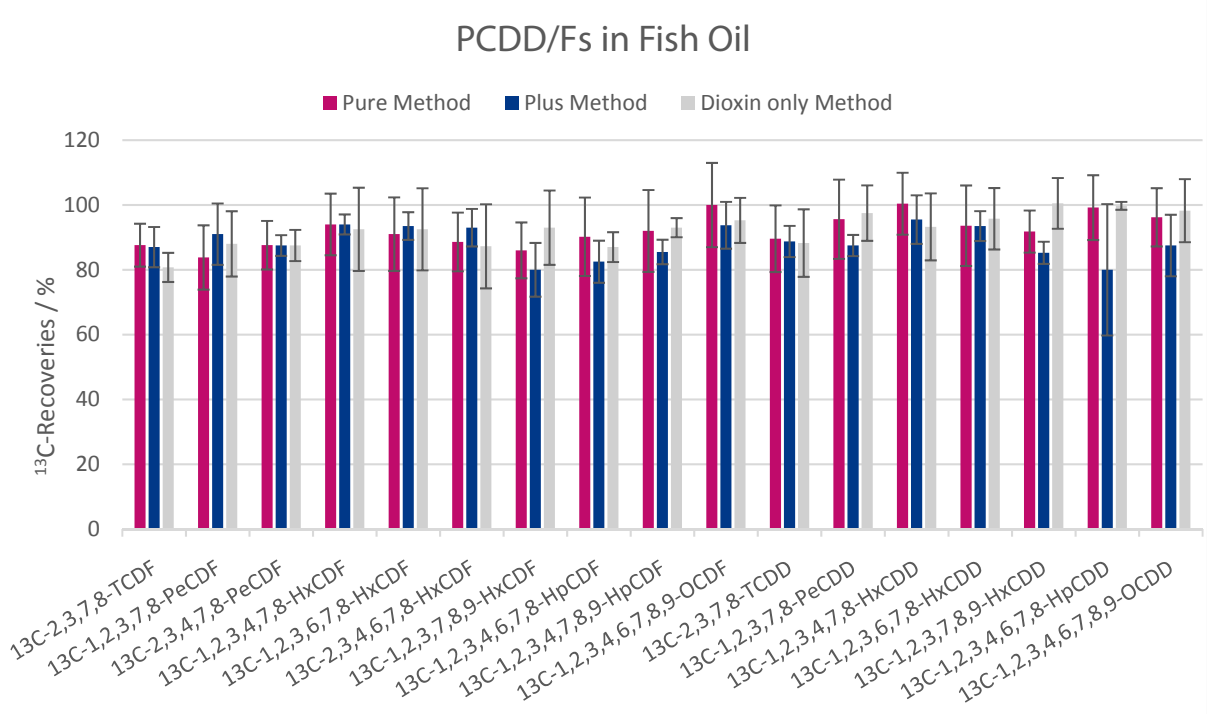
In Table 1 below the different process times, solvent consumptions and fraction volumes are shown.

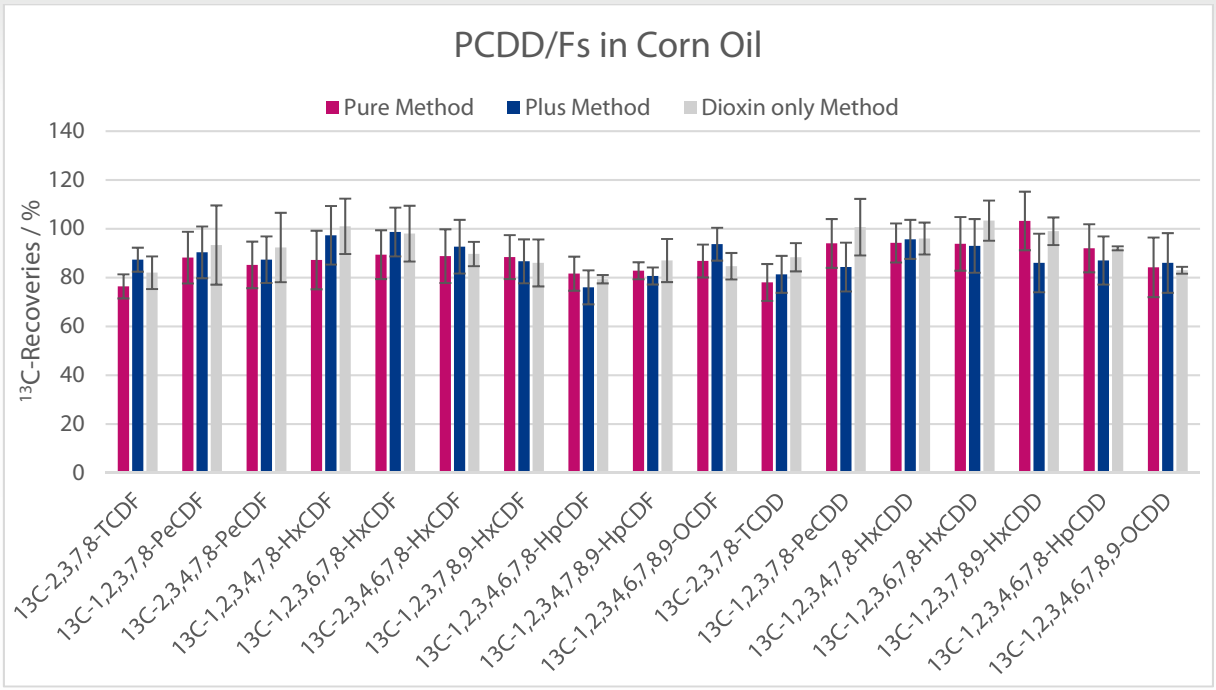
Table 1: Summary of the process times, solvent consumptions and fraction volumes for the different methods on the DEXTech Pure system.

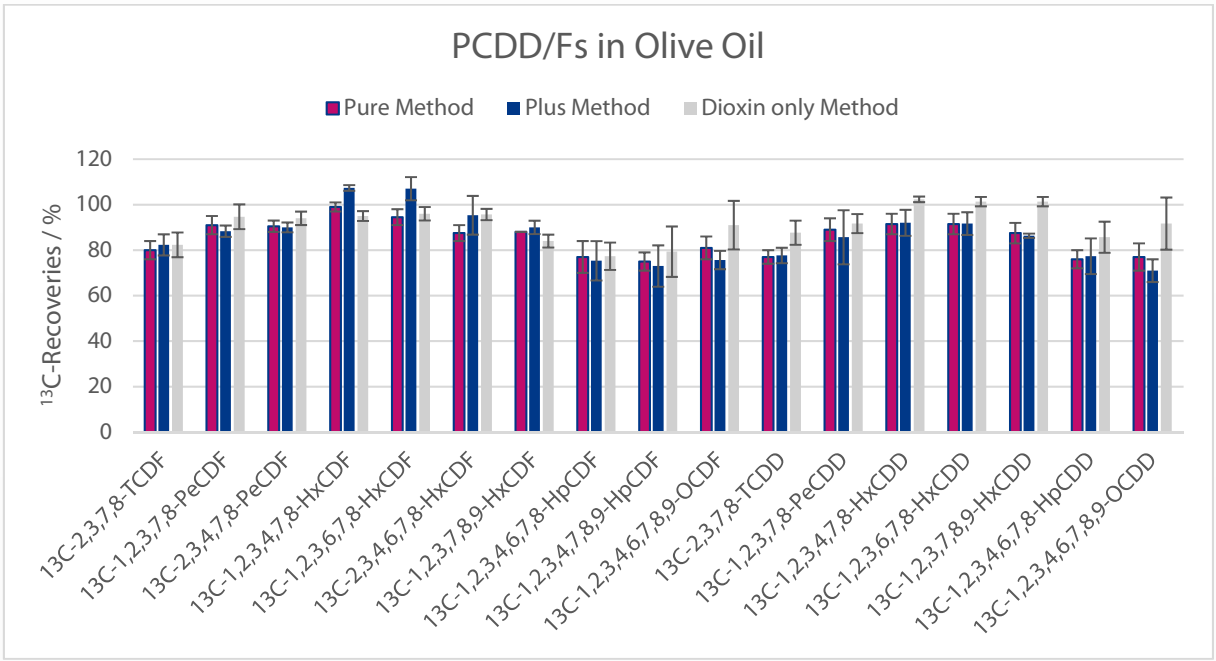
	Alox Pure Method				Alox Plus Method				2 Column PCB Only Method		2 Column Dioxin Only Method	
Column	**Universal**		**SMART**		**Universal**		**SMART**		**Universal**	**SMART**	**Universal**	**SMART**
Process Time	72 min		52 min		65 min		45 min		52 min	32 min	52 min	32 min
Total Solvent Consumption	366 mL		226 mL		342 mL		202 mL		313 mL	164 mL	283 mL	150 mL
Fraction	**F1**	**F2**	**F1**	**F2**	**F1**	**F2**	**F1**	**F2**	**F 1**	**F1**	**F 1**	**F 1**
Fraction Volume in mL	24	10	24	10	24	10	24	10	24	24	10	10

3.5 Comparison of ^{13}C-Recoveries in Different Oil Samples

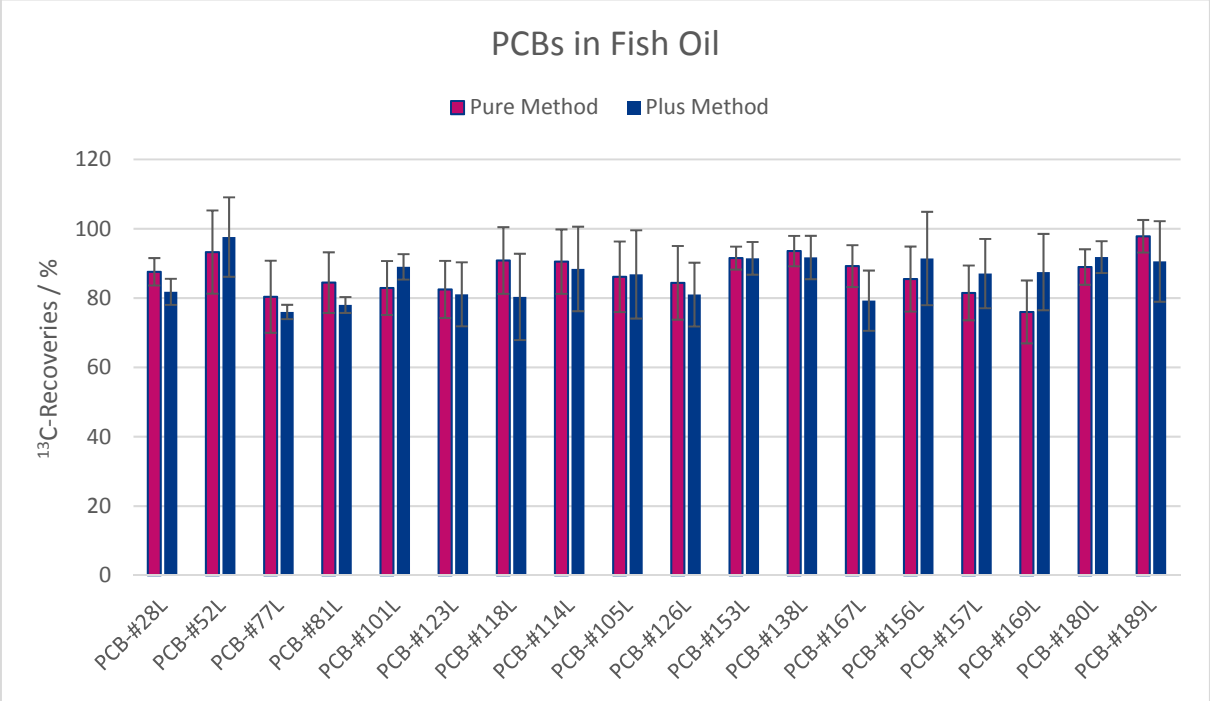
In the following graphs the ^{13}C-recoveries for the PCDD/Fs for different oils processed with the different DEXTech methods are shown.

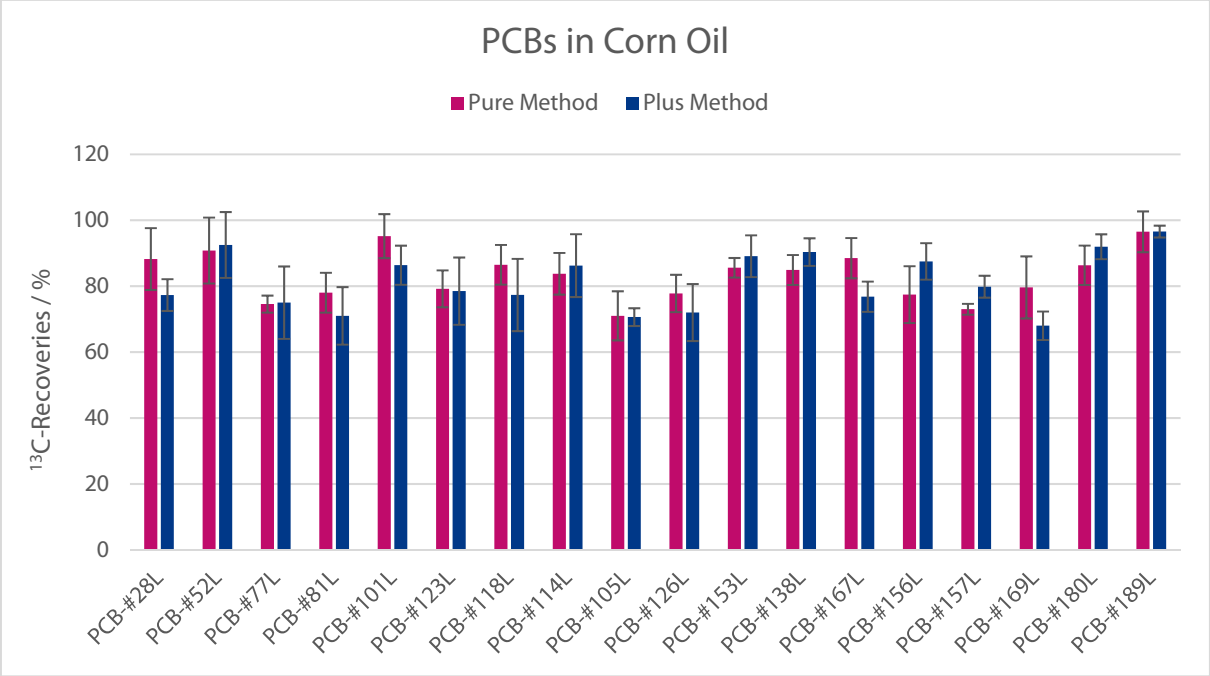


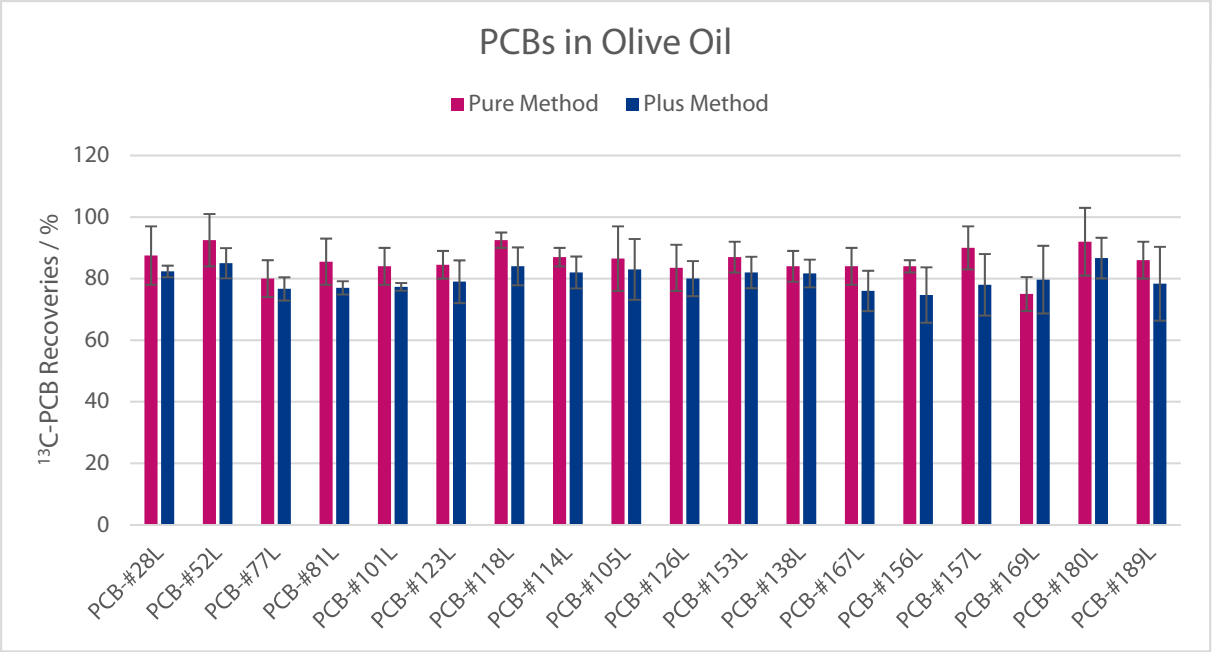

PCDD/Fs in Corn Oil
Pure Method
Plus Method
Dioxin only Method
13C-Recoveries / %
140
120
100
80
60
40
20
0
13C-2,3,7,8-TCDF
13C-1,2,3,7,8-PeCDF
13C-2,3,4,7,8-PeCDF
13C-1,2,3,4,7,8-HxCDF
13C-1,2,3,6,7,8-HxCDF
13C-2,3,4,6,7,8-HxCDF
13C-1,2,3,7,8,9-HxCDF
13C-1,2,3,4,6,7,8-HpCDF
13C-1,2,3,4,7,8,9-HpCDF
13C-1,2,3,4,6,7,8,9-OCDF
13C-2,3,7,8-TCDD
13C-1,2,3,7,8-PeCDD
13C-1,2,3,4,7,8-HxCDD
13C-1,2,3,6,7,8-HxCDD
13C-1,2,3,7,8,9-HxCDD
13C-1,2,3,4,6,7,8-HpCDD
13C-1,2,3,4,6,7,8,9-OCDD


PCDD/Fs in Olive Oil
Pure Method
Plus Method
Dioxin only Method
13C-Recoveries / %
120
100
80
60
40
20
0
13C-2,3,7,8-TCDF
13C-1,2,3,7,8-PeCDF
13C-2,3,4,7,8-PeCDF
13C-1,2,3,4,7,8-HxCDF
13C-1,2,3,6,7,8-HxCDF
13C-2,3,4,6,7,8-HxCDF
13C-1,2,3,7,8,9-HxCDF
13C-1,2,3,4,6,7,8-HpCDF
13C-1,2,3,4,7,8,9-HpCDF
13C-1,2,3,4,6,7,8,9-OCDF
13C-2,3,7,8-TCDD
13C-1,2,3,7,8-PeCDD
13C-1,2,3,4,7,8-HxCDD
13C-1,2,3,6,7,8-HxCDD
13C-1,2,3,7,8,9-HxCDD
13C-1,2,3,4,6,7,8-HpCDD
13C-1,2,3,4,6,7,8,9-OCDD

In the following graphs the PCB ^{13}C-recoveries for different oils processed with the different DEXTech methods are shown.







In all shown experiments above the average recoveries for PCDD/Fs and PCBs range between 63 % and 103 % and are therefore in good agrrement with the legislation requirments of recoveries between 60 % and 120 %.

The results also show that there are essentially no differernces between the different DEXTech methods (Alox Plus, Alox Pure and Dioyin only) in regards to the recoveries of the PCDD/Fs and PCBs.

4. Conclusion

In summary the results shown above proof that the DEXTech systems are very flexible automated clean-up systems, with fast process times and low solvent consumption, satisfying the different needs of routine labs all over the world. The DEXTech systems can either fractionate samples in a pure PCDD/F and PCB fraction or can fractionate the non-ortho-PCBs together with the PCDD/Fs. Therfore, the labs don't have to change their analytical setup when they want to use an automated clean-up system. Additionally, the DEXTech systems offer a cost effective 2-column method if only 1 fraction (either PCB or PCDD/F) is required.

5. 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

Contact

LCTech GmbH
Daimlerstraße 4
84419 Obertaufkirchen
Germany

Tel.: +49 8082 2717-0
Fax: +49 8082 2717-100
E-Mail: info@LCTech.de

www.LCTech.de
www.LCTech-online.com

SOLUTIONS BY LCTech