

DioXin 2018

& 10th International PCB Workshop 26 - 31 August 2018, Kraków, Poland **38th International Symposium on Halogenated Persistent Organic Pollutants (POPs)** Thermo Lunch Seminar: DFS Magnetic Sector GC-HRMS

Krakow, August 26 - 31, 2018

Dual Data Acquisition

Experiences and Application at the CVUA Freiburg / EURL for halogenated POPs

State Institute for Chemical and Veterinary Analysis (CVUA) Freiburg European Union Reference Laboratory (EURL) for Halogenated POPs in Feed and Food Freiburg, Germany

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Content

- Configuration
- Analytes and methods
- Sensitivity and chromatography
- Recoveries of internal standards
- Practical issues





Configuration



- DFS
- 2 x Trace 1310 GC with PTV, SSL injector
- 2 x TriPlus RSH
- Dual Data XL

(Installation: end of 2016)





Configuration

- Instrument methods
 - Alternating staggered **Dual Data Sequence**

Run Parameter						
Method Type	dual (alternating)	•	Start Device	1	•	
			Valves Mode	with Valves	-	
			Injection by	Autosampler	•	

Single Sequences (only one side) with micro fluidic channel device (MCD)

Run Parameter	r					
Method Type	single	•	Start Device	1	•	ă.
			Valves Mode	with Valves	Ŧ	
			Injection by	Autosampler	•	

Single Sequences (only one side) with column direct into ion source (without MCD)

Writhout Type single Image: Start Device Image: Start Device Image: Start Device Valves Mode without Valves Image: Start Device Image: Start Device Injection by Autosampler Image: Start Device	nical a of Food g	Analysis of A Freiburg	Veterinary A CVUA	* *	Laboratory	n Reference	European Union				
				• *	iout Valves osampler	e witi Au	Start Device Valves Mode Injection by	*	single	thod Type	Me



Configuration







Analytes of interest

- Current **analytes of interest** on Dual Data XL DFS:
 - PCDD/Fs
 - PCBs
 - NDL-PCBs (indicator PCBs)
 - WHO-PCBs
 - mono-ortho-PCBs
 - non-ortho-PCBs
 - PBDEs
- Extracts for GC-HRMS measurement:
 - (1) PCDD/Fs
 - (2) non-ortho-PCBs
 - (3) mono-ortho-PCBs + indicator PCBs
 - (4) PBDEs





Methods

PCDD/Fs

Injektor	PTV, 5 µl injection (solvent vent)
Column	DB-5MS (60m, 0.25 mm ID, 0.25 µm film) Flow: 1.5 ml/min
GC run time	ca. 36 min

Mono-ortho-PCBs + Indicator PCBs

Injektor	SSL, 1 µl splitless injection
Column	MXT-500 (60m, 0.25 mm ID, 0.15 µm film) Flow: 1.5 ml/min
GC run time	ca. 40 min



Non-ortho-PCBs

Injektor	SSL, 1 µI splitless injection						
Column	DB-5MS (60m, 0.25 mm ID, 0.25 µm film) Flow: 1.5 ml/min						

GC run time ca. 38min





Methods

PBDEs

Injektor	PTV, 5 µl injection (solvent vent)
Column	RTX-5 (15m , 0.25 mm ID, 0.25 µm film) Flow: 2.0 ml/min
GC run time	ca. 30 min

Injektor	SSL, 1 µl splitless injection
Column	RTX-5 (7m , 0.25 mm ID) Flow: 4.0 ml/min
GC run time	ca. 16 min







Dual Data Acquisition

Dual data acquisition:

- PCDD/Fs + PCDD/Fs
- PCDD/Fs + non-ortho-PCBs
- Mono-ortho-PCBs/Indicator PCBs + non-ortho-PCBs
- PCDD/Fs + PBDEs (15m, 7m column)







Dual Data Acquisition





Sensitivity and chromatography



Sensitivity (20 fg 2,3,7,8-TCDD)





Sensitivity and chromatography







Recoveries of internal standard

- Calculation of receiveries of ratio of recovery standard(s) and internal standards
- Reeovery standard(s) for PCDD/Fs:
 - Originally ¹³C₁₂-1,2,3,4-TCDD
 - Since 2017: Multi-standard with recovery standard for each chlorination degree for dioxins and furans

 ${}^{13}C_{12}-1,2,7,8-TCDF$ ${}^{13}C_{12}-1,2,3,4-TCDD$ ${}^{13}C_{12}-1,2,3,4,6-PeCDF$ ${}^{13}C_{12}-1,2,3,4,7-PeCDD$ ${}^{13}C_{12}-1,2,3,4,6,9-HxCDF$ ${}^{13}C_{12}-1,2,3,4,6,8-HxCDD$ ${}^{13}C_{12}-1,2,3,4,6,8,9-HpCDF$ ${}^{13}C_{12}-1,2,3,4,6,7,9-HpCDD$





Recoveries of internal standard

Runs with column direct in source (without MCD) 08-direkt 0 11-direkt 0 12-direkt 0 15-direkt 0 16-direkt 0 100 % Recoveries Recoveries Recoveries Recoveries 7777777777777

Runs with MCD



Runs with MCD (Calculation with Multi-Std.)



Practical issues

- Setup of sequence list
- GC column exchange
- Handling of the MCD wafer in routine
- Potential leakage
- Cleanliness / contamination of source





Sequence setup

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s Acquisition Queue	37	Unknown	cdx_100517-19	170266814	Drawer 1:Slot2:3	8301	Lammschulter_8301	2.000 8.8	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
Al Sequences	38	Unknown	bde_100517-19		Drawer 1:Slot1:1	K1	BDE K_1	3.000	C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
IHOMEPAGEI - C:\Xcalibur\Data\ cdx\c	39	Unknown	cdx_100517-20	170270536	Drawer 1:Slot2:4	8302	Lammfleisch_8302	2.000 15.3	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
Sequence Row #1	40	Unknown	bde_100517-20	Stdd. Unep	Drawer 1:Slot1:49	a s	PBDE-Stdd. Unep 2016_S	1.000	C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
- 🐼 👖 Sequence Row #2	41	Unknown	cdx_100517-21	170276081	Drawer 1:Slot2:5	8305	Lammfleisch Keule_8305	2.000 5.9	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
Sequence Row #3	42	Unknown	bde_100517-21		Drawer 1:Slot1:10	D LM	Cyclohexan_LM	3.000	C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
	43	Unknown	cdx_100517-22	10007682-052	Drawer 1:Slot2:6	Q	QK 7, 04.05.17 RT zu Dorschleber/Fleisch_Q	1.500	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
🐼 📋 Sequence Row #5	44	Unknown	bde 100517-22	BW	Drawer 1:Slot1:50) t	Reagentien-BW, 01.04.16 RT t	3.000 100	C:\Xcalibur\Data\ bde\bde 100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
- 🚫 🚺 Sequence Row #6	45	Unknown	cdx 100517-23		Drawer 1:Slot1:4	E4L	Eich 4L	3.000	C:\Xcalibur\Data\ cdx\cdx 100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
🐼 🚺 Sequence Row #7	46	Unknown	bde 100517-23		Drawer 1:Slot1:3	К3	BDE K 3	3.000	C:\Xcalibur\Data\ bde\bde 100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
- 🐼 🚺 Sequence Row #8	47	Unknown	cdx 100517-24		Drawer 1:Slot1:10	D LM	Toluol LM	3.000	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	
Sequence Row #9	48	Unknown	bde 100517-24	A	Drawer 1:Slot1:51	F	Fish-Oil Best A. t	3,000 100	C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-EC5311-dd2 meth	
Sequence Row #10	49	Unknown	cdx 100517-25	170270695	Drawer 1:Slot2:7	8295	Dorschleher in eigenem Saft 8295	2 000 58	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibu:\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-EC5311-dd2 meth	
Sequence Row #11	50	Unknown	bde 100517-25	B	Drawer 1:Slot1:52	2	Fish-Oil Best B t	3,000,100	C:\Xcalibur\Data_bde\bde_100517	C/Xcalibut\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-EC5311-dd2 meth	
Sequence Row #12	51	Unknown	cdx 100517-26	170275295	Drawer 1:Slot2:8	8297	Dorschleber im eigenen Saft und ÖL 8297	2,000,61,9	C\Xcalibur\Data_cdx\cdx_100517	C\Xcalibut\methods\cdv\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-EC5311-dd2 meth	
- Sequence Row #13	52	Unknown	bde 100517-26	110210200	Drawer 1:Slot1:5	K5	BDE K 5	3,000	C\Xcalibur\Data_bde\bde_100517	C\Xcalibu\methods\cdvbdefull-db5-30-SSL-diovfull-db5-60-PTV-EC5311-dd2 meth	
Sequence Row #14	53	Unknown	cdv 100517-27	170275296	Drawer 1:Slot2:9	8298	Dorschleber im eigenen Saft und ÖL 8298	2,000 61.1	C\Xcalibur\Data_cdx\cdx_100517	C\\/calibus\methods\cdv\bdefull-db5-30.SSL-diovfull-db5-60-PTV-EC5311-dd2 meth	
Sequence Row #15	54	Unknown	bde 100517-27	110210200	Drawer 1:Slot1:10	1 1 M	Euclohevan I.M	3,000	C:Vcalibur/Data_bde\bde_100517	C:\Vcalibus\methods\cdx\bdefull.db530.SSL.diovfull.db560.PTV/FC5311.dd2.meth	
Sequence Row #15	55	Unknown	cdv 100517-28	170270563	Drawer 1:Slot2:10	1 8293	10 frische Fier 8293	2,000 8.9	C:Vcalibur/Data_cdx/cdx_100517	C:\Vcalibus\mathcds\cdx\bdefull.db530.SSL.diovfull.db5.60.PTV-FC5311.dd2.meth	
Sequence Row #17	56	Unknown	bde_100517-28	r	Drawer 1:Slot1:53	1 1	Fish-OilBest C 1	3,000 100	C:\Vcalibur\Data_bde\bde_100517	C:\Vealibur\mathods\cdx\bdafull.db530.55E.doxfull.db560.PT\/FC5311.dd2.math	
AND Common Row #10	57	Unknown	adv 100517-20	0	Drawer 1.Clat1.1	C 11	Fish 11	3.000 100	C: VealburtDatal_bde/bde_100317	C/V a libra v analyzed a day la day of discus des 20,000 discus de 20,000 million de 20,0000 million de 20,000 million de 20,000 million de 20,000 million d	
Sequence now #19	58	Unknown	bdo 100517-23	D	Drawer 1:Slot1:5/	1.6	Eich Oil Post D. J.	2,000 100	C.V.CaliburyData_c0x100x17	C. Vycalibu/ methoda) odu) bdofull db5 20 CCL dioufull db5 20 DTV/ EC311 dd2 meth	
Sequence Row #20	50	Unknow	adu 100517-23	170270522	Drawer 1.Stot1.54	0100	10 Erisaka Eise 0000	2,000 7.0	C. V. Calibury Data Lode Lode 100517	C. Vscalbur methods adult adult idae 20 CCL david idae 20 DTV 505244, 420	
Sequence now #21	60	Unknown	Cax_100517-30	0270000	Drawer 1:510(2:1	0236		2.000 7.0	C.V.Caliburi/Datas_cox.cox_100517	C. Vycaliour Virenous (Cax) back (Lake 30 CC), Reveal are constructed and a state of V = 0, and a state and back (Lake 30 CC), Reveal are constructed and a state of V = 0. The state and back (Lake 30 CC).	
Sequence Row #22	61	Unknown	Due_100517-30	Seti		r et	andered si	annehí	<u>naras</u>	S 2 1 V stock back in the sole of the sole	
Sequence Row #23	67	Unknown	Cax_100517-31	0011				yuu un		may as cax baeruir abo-su-SSL-dioxtull-db5-60-PTV-FL53T1-dd2.meth	
- Roll Sequence Row #25	62	Unknown	bde_100517-31	* 7000* 000	Lawer 1:Slot1:4	K4	BDE A A A A A A A A A A A A A A A A A A A	1 0.000	L:vscalibur/Data/_bde/bde_100517	L: Vscalibur / new oos/cax/baeruii-abo-su-5SL-dioxtuli-db5-60-PTV-FU5311-dd2.meth	
Sequence Row #26	63	Unknown	cdx_100517-32	170281880	Drawer 1:Slot2:13	3 8306	Lier aus Bodennaltung_8306	2.000 8.5	L:vscalibur\Data_cdx\cdx_100517	U:VsCalibur/methods/cdx/bdetuil-dbb-30-5SL-dioxtull-dbb-60-PTV-FU5311-dd2.meth	
Sequence Bow #27	64	Unknown	bde_100517-32		Drawer 1:Slot1:10	U LM	Lyclohexan_LM	3.000	L:\Xcalibur\Data_bde\bde_100517	U:VXcalibur\methods\cdx\bdefull-db5-3U-SSL-dioxfull-db5-6U-PTV-FC5311-dd2.meth	
X *	65	Unknown	Lodx 100517-33	170285193	Drawer 1:Slot2:14	1 8307	Huhnereier 8307	2.000 7.9	E:\Xcalibur\Data_cdx\cdx_100517	E:\Xcalibur\methods\cdx\bdetull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth	

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bde_100517-20	Stdd. Unep	Drawer 1:Slot1:49	S	PBDE-Stdd. Unep 2016_S	1.000		C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
cdx_100517-21	170276081	Drawer 1:Slot2:5	8305	Lammfleisch Keule_8305	2.000	5.9	C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
bde_100517-21		Drawer 1:Slot1:10	LM	Cyclohexan_LM	3.000		C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
cdx_100517-22	10007682-052	Drawer 1:Slot2:6	Q	QK 7, 04.05.17 RT zu Dorschleber/Fleisch_Q	1.500		C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
bde_100517-22	BW	Drawer 1:Slot1:50	t	Reagentien-BW, 01.04.16 RT_t	3.000	100	C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
cdx_100517-23		Drawer 1:Slot1:4	E4L	Eich_4L	3.000		C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
bde_100517-23		Drawer 1:Slot1:3	КЗ	BDE K_3	3.000		C:\Xcalibur\Data_bde\bde_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth
cdx_100517-24		Drawer 1:Slot1:10	LM	Toluol_LM	3.000		C:\Xcalibur\Data_cdx\cdx_100517	C:\Xcalibur\methods\cdx\bdefull-db5-30-SSL-dioxfull-db5-60-PTV-FC5311-dd2.meth

- Manual setup of DualData sequence lists with Xcalibur Sequence Setup more complex and time-consuming than forsingle sequences
- Setup in Excel and import in Xcalibur highly recommended





GC column exchange

- Column changing possible without venting the ion source and cooling down the ion source and the transfer line
- Increase of helium flow during column exchange
- > No significant air entrance into ion source
- No significant negative effects on ion source vacuum





GC column exchange



Handling in routine

Additional connections and tubings for Dual Data



Handling in routine

MCD wafer with 4 connectors



Halogenated POPs

Potential leakage





Additional possible leakage

Problematic leakage source (also without dual data)







- DFS in Dual Data acquisition mode routinely applied for PCDD/Fs, PCBs and PBDEs
- Considerably higher sample throughput possible
- No negative effects on sensitivity, chromatography or recoveries observed
- User-friendly setup of Dual Data methods (high flexibility)
- Sequence setup and handling in routine more complex
- Additional leakage sources





Thank you very much for your attention !

Contact: eurl-dioxin@cvuafr.bwl.de



