



UNIUNEA EUROPEANĂ



GUVERNUL ROMÂNIEI



**Programul Operational Sectorial
"Creșterea Competitivității Economice"
co-finantat prin
Fondul European de Dezvoltare Regională
"Investiții pentru viitorul dumneavoastră"**

**INFRASTRUCTURA MULTISITE PENTRU
CREȘTEREA CAPACITĂȚII DE CERCETARE ȘI INOVARE
ÎN DOMENIUL OPTOELECTRONICII ȘI INSTRUMENTAȚIEI
ANALITICE**

INOVA-OPTIMA



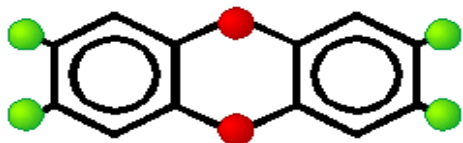
Analiza dioxinelor și furanilor prin tehnica GC-MS/MS cu diluție izotopică

Mirela Miclean, Melinda-Haydee Kovacs, Dalma Kovacs

INCDO-INOE 2000, Institutul de Cercetari pentru
Instrumentatie Analitica



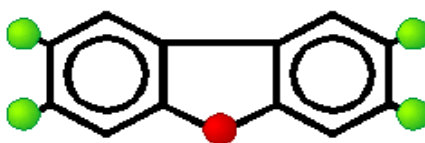
Dioxine și compuși asemănători dioxinelor



2,3,7,8-TetraCDD

Dioxine (PCDD)
75 congeneri
7 toxici

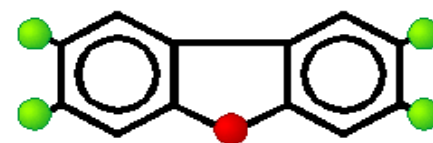
2,3,7,8-TCDD !!
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8,9-OCDD



2,3,7,8-TetraCDF

Furani (PCDF)
135 congeneri
10 toxici

2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
1,2,3,4,6,7,8,9-OCDF

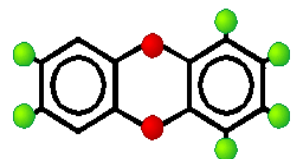


One of 209 PCBS

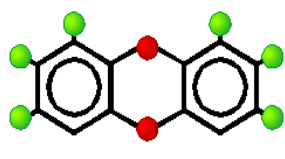
PCB
209 congeneri
12 toxici

3,3',4,4'-TeCB
3,4,4',5-TeCB
2,3,4,5-TeCB
3,3',4,4',5-PeCB
2,3,3',4,4'-PeCB
2,3',4,4',5-PeCB
3,3',4,4',5,5'-HxCB
2,3,3',4,4',5-HxCB
2,3,3',4,4',5-HxCB
2,2',3,4,4',5'-HxCB
2,2',3,3',4,4',5-HpCB

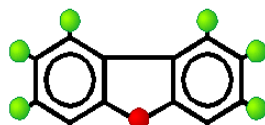
Dioxine și furani extrem de toxici



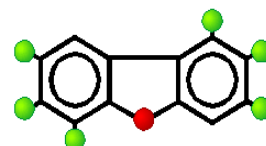
1,2,3,4,7,8-HexaCDD



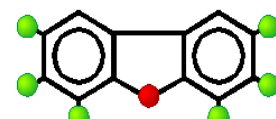
1,2,3,7,8,9-HexaCDD



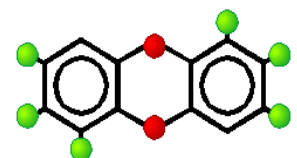
1,2,3,7,8,9-HexaCDF



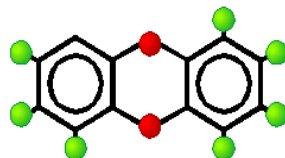
1,2,3,6,7,8-HexaCDF



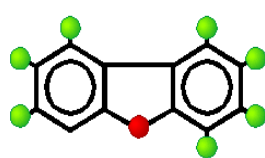
2,3,4,6,7,8-HexaCDF



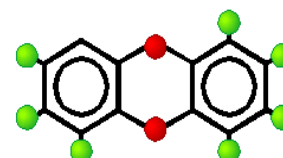
1,2,3,6,7,8-HexaCDD



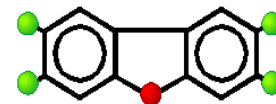
1,2,3,4,6,7,8-HeptaCDD



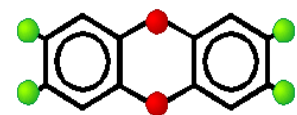
1,2,3,4,7,8,9-HeptaCDF



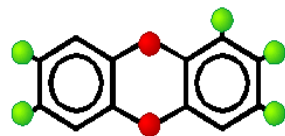
1,2,3,4,6,7,8-HeptaCDD



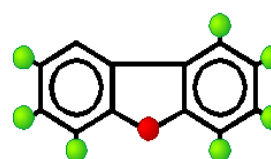
2,3,7,8-TetraCDF



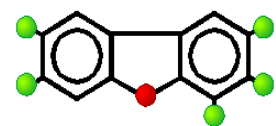
2,3,7,8-TetraCDD



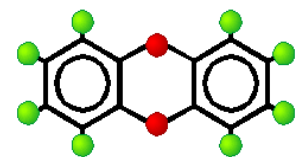
1,2,3,7,8-PentaCDD



1,2,3,4,6,7,8-HeptaCDF

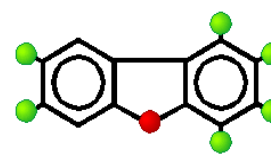


2,3,4,7,8-PentaCDF

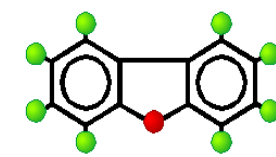


OctaCDD

**2,3,7,8-Tetraclorodibenzo-
p-dioxina**
***“Compusul cel mai toxic
produs vreodată de om”***



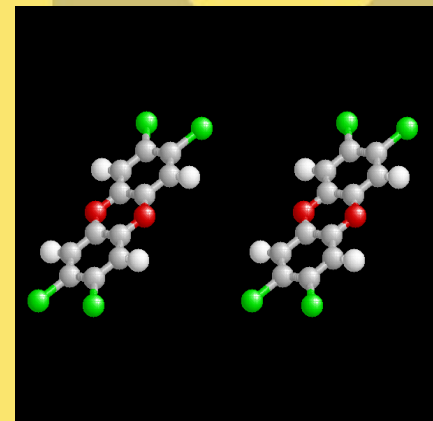
1,2,3,4,7,8-HexaCDF



OctaCDF

Dioxine și compuși asemănători dioxinelor

- Contaminanți de mediu
- Extrem de toxici
- Semivolatili
- Lipofili (se acumulează în țesuturile grase)
- Hidrofobi
- Persistenți în mediu
- Bioacumulativi
- Se concentrează în lanțurile trofice



Dioxine și compuși asemănători dioxinelor

Concentrații ultra-urme

- Sol, alimente: ppt (ng/kg) ($1 \text{ ng} = 10^{-9} \text{ g}$)
- Apă: ppq (pg/l) ($1 \text{ pg} = 10^{-12} \text{ g}$)
- Aer: fg/m³ ($1 \text{ fg} = 10^{-15} \text{ g}$)
- Ser: ppt
- Aport prin ingerare: 1 pg/kg/TEQ
- Risc de cancer: 1×10^{-3}





Toxicitatea dioxinelor

- Toxice puternice pentru organismul uman și animal
- Mecanism toxic comun: alterează creșterea și dezvoltarea celulară
- Efecte:
 - reproductiv
 - circulator
 - imunologic
 - cancerigen



Viktor Yushchenko (Ucraina)
(înainte și după expunere)

Populația vulnerabilă: nou-născuții și copii!



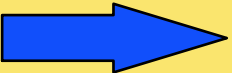
Surse și căi de pătrundere în organismul uman

- Sursa principală (în organismul uman): alimentele, în particular lipidele animale
- Sursa principală (în mediu): procesele de combustie (incinerarea reziduurilor medicale, municipale, toxice; topirea metalelor; combustii industriale)
- Căi de pătrundere în organism:
 - ingestie,
 - inhalare,
 - contact dermic,
 - transplacentară,
 - alăptare.



Surse și căi de expunere

SURSE


TRANSPORT

DEPUNERE

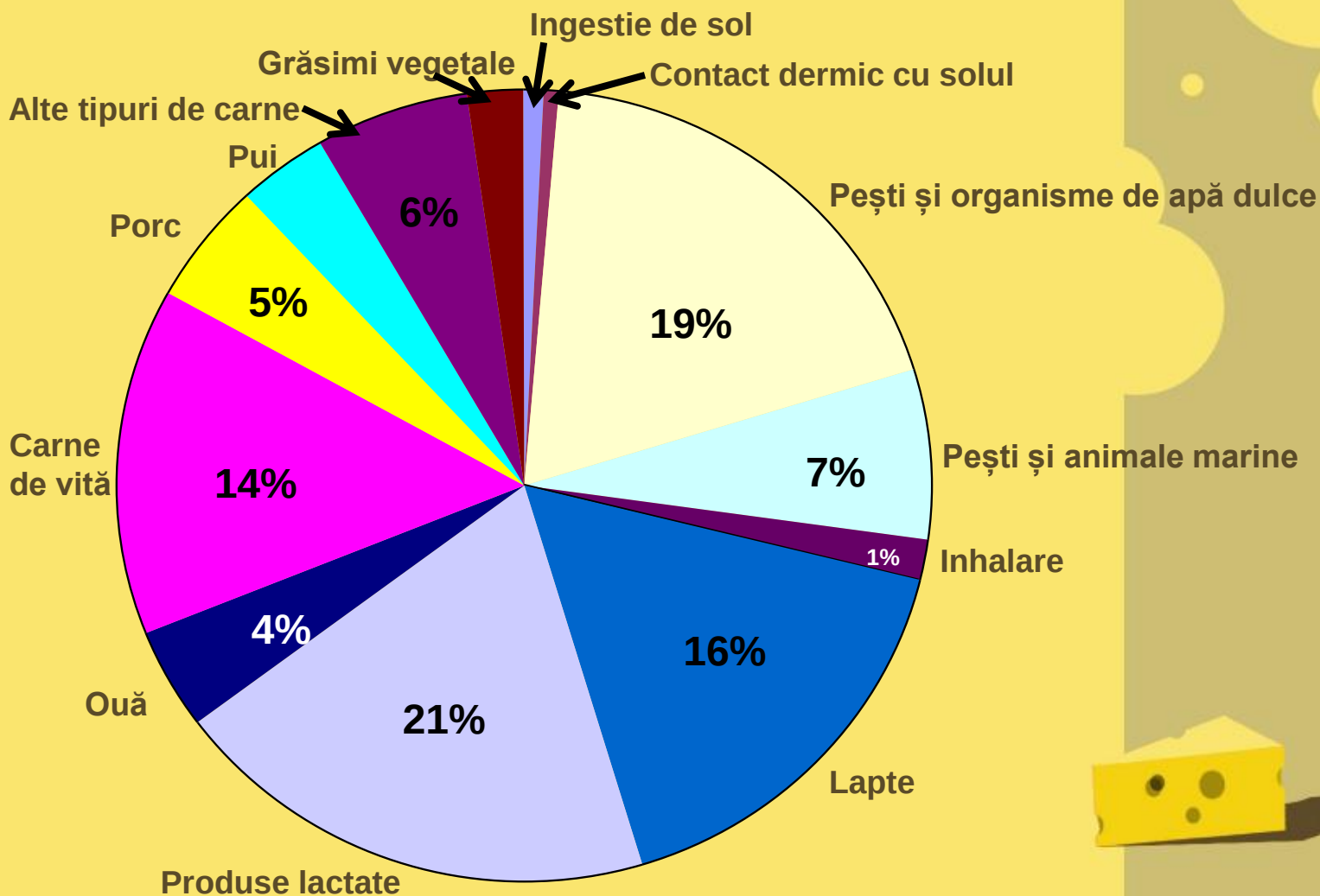
ALIMENTE



**Drenaj
Eroziune**



Expunerea organismului uman la dioxine prin consumul de alimente



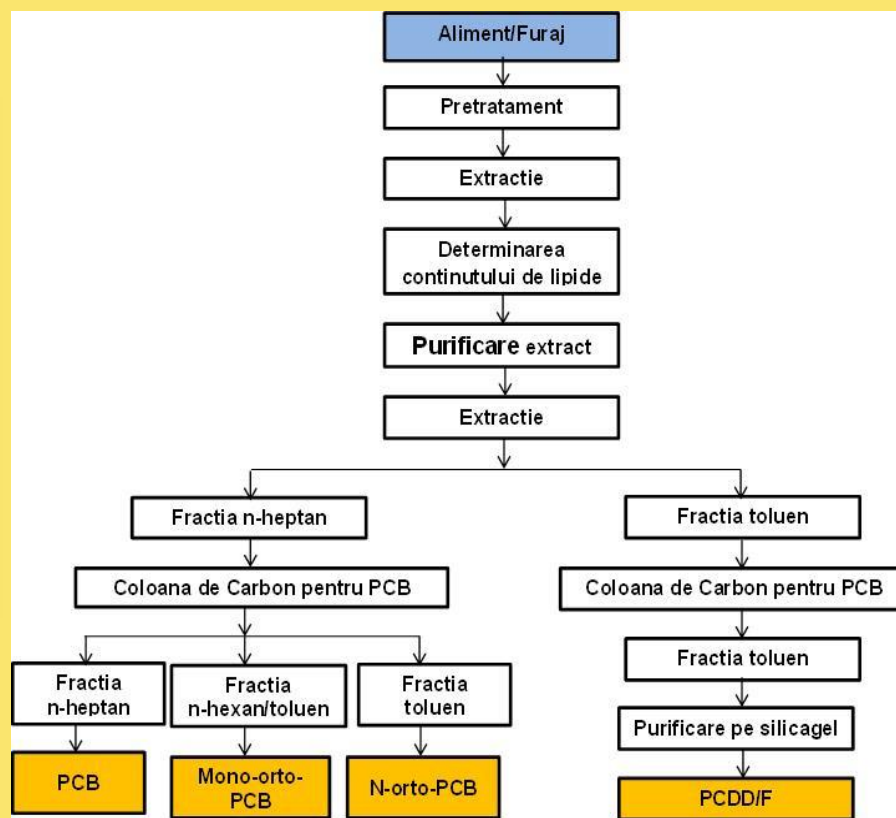
Analiza GC-MS/MS a dioxinelor și a compușilor asemănători dioxinelor din probe de alimente



Extracția și purificarea probei de aliment pentru determinarea PCDD/F și PCB



Sistem de extracție accelerată cu solvenți
Thermo Scientific™
Dionex™ ASE™ 350
(dotare ICIA)



Sistem de purificare automată
LCTech DEXTech™
(dotare ICIA)



Sistem GC TRACE™ 1310 cuplat cu spectrometru de masă triplu cuadrupol TSQ 8000 Evo GC-MS/MS Thermo Scientific™, cu autosampler Thermo Scientific™ TriPlus™ RSH și coloană capilară Thermo Scientific™ TraceGOLD TG-5SilMS 60 m × 0.25 mm I.D. × 0.25 μm film (*dotare ICIA*)

Tabel 1. Condiții instrumentale pentru GC și injector

Injector PTV	
Volum de injecție (μL)	2
Liner	SSL Single taper
Inlet (°C)	260
Debit de vent	20 ml/min
Rata de transfer (°C/min)	13.3
Mod Inlet	Splitless
Program de temperatura pentru cuptorul GC TRACE 1310	
Coloană capilară GC	TraceGold TG-5SilMS, 60 m x 0,25 mm x 0,25 um
Temperatură inițială (°C)	120
Rata 1	17 °C/min la 250 °C
Rata 2	2.5 °C/min la 285 °C
Temperatură finală	285 °C pentru 13 min

Exemplu de soluții de calibrare pentru metoda EN1948

NATIVE PCDDs & PCDFs	1948CS1 (pg/μl)	1948CS2 (pg/μl)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	0.2	0.8
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	0.4	1.6
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0.4	1.6
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0.4	1.6
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	0.4	1.6
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0.8	3.2
Octachlorodibenzo-p-dioxin	0.8	3.2
2,3,7,8-Tetrachlorodibenzofuran	0.2	0.8
1,2,3,7,8-Pentachlorodibenzofuran	0.4	1.6
2,3,4,7,8-Pentachlorodibenzofuran	0.4	1.6
1,2,3,4,7,8-Hexachlorodibenzofuran	0.4	1.6
1,2,3,6,7,8-Hexachlorodibenzofuran	0.4	1.6
1,2,3,7,8,9-Hexachlorodibenzofuran	0.4	1.6
2,3,4,6,7,8-Hexachlorodibenzofuran	0.4	1.6
1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.8	3.2
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.8	3.2
Octachlorodibenzofuran	0.8	3.2

SAMPLING STANDARDS

1,2,3,7,8-Pentachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,7,8,9-Hexachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,4,7,8,9-Heptachloro[¹³ C ₁₂]dibenzofuran	32	32

EXTRACTION STANDARDS

2,3,7,8-Tetrachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16
2,3,7,8-Tetrachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,7,8-Pentachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16
2,3,4,7,8-Pentachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,4,7,8-Hexachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16
1,2,3,6,7,8-Hexachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16
1,2,3,4,7,8-Hexachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,6,7,8-Hexachloro[¹³ C ₁₂]dibenzofuran	16	16
2,3,4,6,7,8-Hexachloro[¹³ C ₁₂]dibenzofuran	16	16
1,2,3,4,6,7,8-Heptachloro[¹³ C ₁₂]dibenzo-p-dioxin	32	32
1,2,3,4,6,7,8-Heptachloro[¹³ C ₁₂]dibenzofuran	32	32
Octachloro[¹³ C ₁₂]dibenzo-p-dioxin	32	32
Octachloro[¹³ C ₁₂]dibenzofuran	32	32

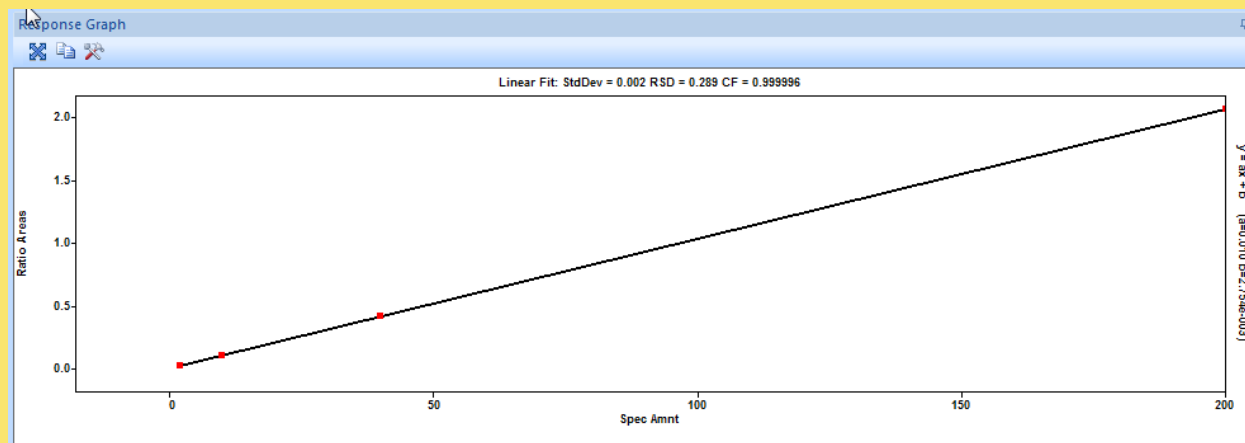
SYRINGE STANDARDS

1,2,3,4-Tetrachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16
1,2,3,7,8,9-Hexachloro[¹³ C ₁₂]dibenzo-p-dioxin	16	16

Rezultate obținute

Sequence View

	RawFile	Process Status	Sample Nam	Sample Id	Sample Type	Resp Mode	Response File	Method File	Smp Weight	Smp Vol	Dilution Factor
	cs2_test	processed		1	Std Clear	Single Point (	Calibration1500708a	cs2_test	1.0000	1.0000	1.0000
	cs3_test	processed		1	Std Clear	Single Point (	Calibration1500708a	cs2_test	1.0000	1.0000	1.0000
	cs4_test	processed		1	Std Clear	Single Point (	Calibration1500708a	cs2_test	1.0000	1.0000	1.0000
	cs5_test	processed		1	Std Clear	Single Point (	Calibration1500708a	cs2_test	1.0000	1.0000	1.0000
	cs_test_ur	processed		1	Unknown	Average RF	Calibration1500708a	cs2_test	1.0000	1.0000	1.0000



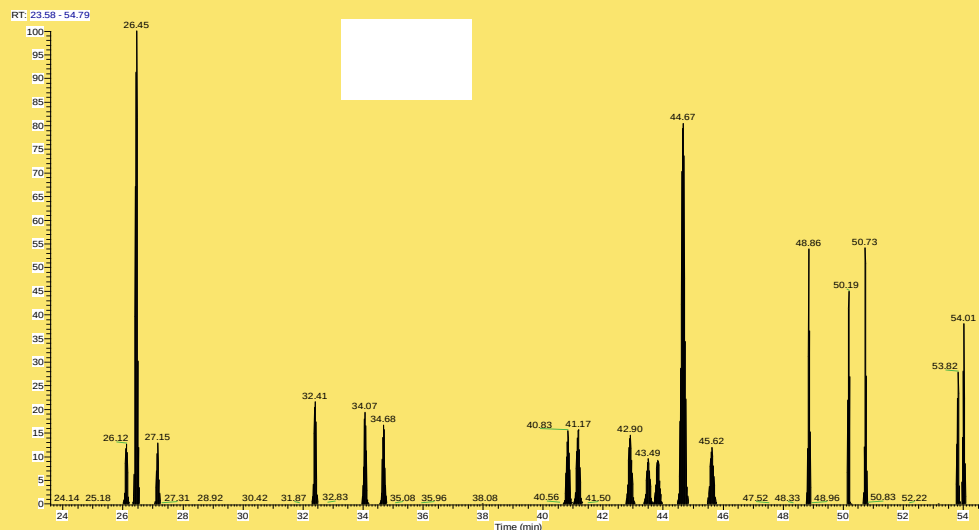
Secvența și curba de calibrare



Ciocolată



No.	Compound Name	QM Retention Time	QM Area	RM1 Area	RM1 Ratio (A)	Calculated Amount (A)	Detection Limit (A)	TEQ (A)
1	2378-TCDD	0.00	0	0	---	n.d.	0.04	n.d.
2	12378-PeCDD	34.71	2041	960	0.4703	0.53	0.03	0.5268
3	123478-HxCDD	43.52	1414	815	0.5764	0.37	0.07	0.0371
4	123678-HxCDD	43.85	1473	1012	0.6871	0.49	0.09	0.0490
5	123789-HxCDD	44.68	2485	0	0.0000	n.d. < 0.47	0.09	n.d.
6	1234678-HpCDD	50.20	4375	3159	0.7219	0.63	0.01	0.0063
7	OCDD	53.84	13673	13743	1.0051	5.89	0.06	0.0018
8	2378-TCDF	26.13	458	1677	3.6619	n.d. < 0.36	0.05	n.d.
9	12378-PeCDF	32.44	3506	655	0.1867	n.d. < 0.59	0.07	n.d.
10	23478-PeCDF	34.10	3916	1607	0.4104	0.78	0.07	0.2338
11	123478-HxCDF	40.88	2295	1370	0.5970	0.44	0.04	0.0443
12	123678-HxCDF	42.93	1719	1173	0.6825	0.34	0.04	0.0343
13	234678-HxCDF	42.93	1860	1173	0.6306	0.36	0.04	0.0359
14	123789-HxCDF	45.65	1957	1316	0.6722	0.44	0.05	0.0443
15	1234678-HpCDF	48.87	2360	2070	0.8769	0.29	0.02	0.0029
16	1234789-HpCDF	50.75	5424	4663	0.8598	0.70	0.02	0.0070
17	OCDF	54.03	10331	11532	1.1162	3.11	0.03	0.0009
18	Overall_TEQ	0.00	52840	44594	0.8439	14.37	0.04	1.0245



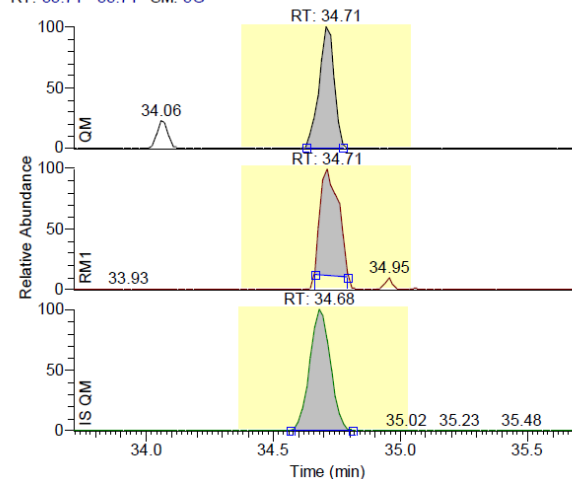
NL: 2.06E6
TIC: MS
chocolate

chocolate_seq acquired 2015/10/16 15:12

SampleName: Id: 1 Comment:
Study: Client:

Chromatogram

RT: 33.71 - 35.71 SM: 5G



NL: 4.97E2
m/z= 292.880-292.900 F: + c
EI SRM ms2
355.850@cid20.00
[292.885-292.895] MS ICIS
chocolate

NL: 2.19E2
m/z= 294.880-294.900 F: + c
EI SRM ms2
357.850@cid20.00
[294.885-294.895] MS ICIS
chocolate

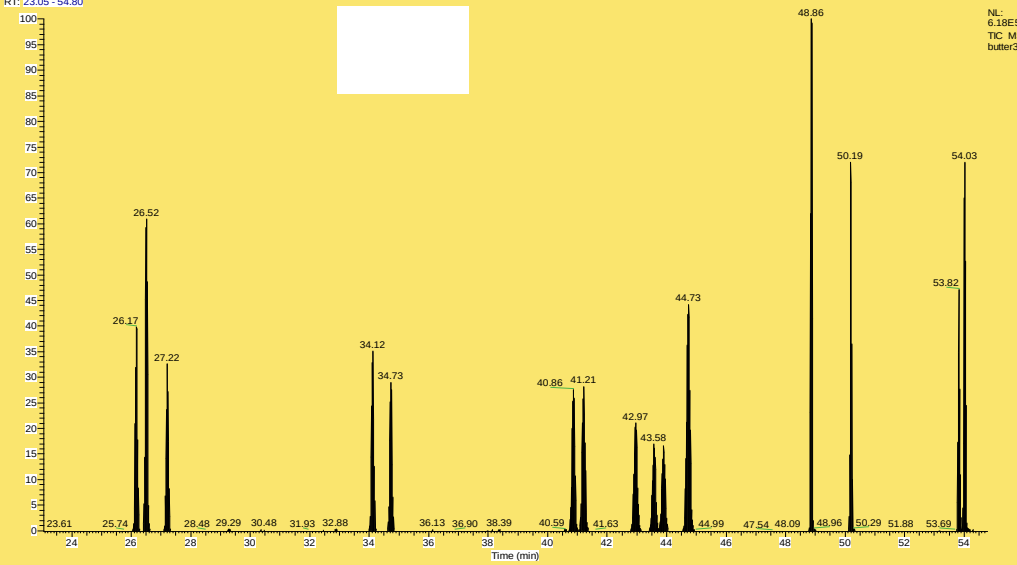
NL: 3.22E5
m/z= 303.920-303.940 F: + c
EI SRM ms2
367.890@cid22.00
[303.925-303.935] MS ICIS
chocolate

Unt

No.	Compound Name	QM Retention Time	QM Area	RM1 Area	RM1 Ratio (A)	Calculated Amount (A)	Detection Limit (A)	TEQ (A)
1	2378-TCDD	0.00	0	0	---	(A)	0.01	n.d.
2	12378-PeCDD	34.76	1229	663	0.5392	n.d.	0.01	0.1960
3	123478-HxCDD	43.64	898	258	0.2876	0.20	0.03	n.d.
4	123678-HxCDD	43.96	570	258	0.4532	n.d. < 0.12	0.04	n.d.
5	123789-HxCDD	44.76	600	0	0.0000	n.d. < 0.10	0.04	n.d.
6	1234678-HpCDD	50.22	3931	2896	0.7367	n.d. < 0.07	0.01	0.0036
7	OCDD	53.85	3531	3626	1.0271	0.36	0.03	0.0003
8	2378-TCDF	26.18	1650	0	0.0000	0.91	0.01	n.d.
9	12378-PeCDF	32.45	2148	0	0.0000	n.d. < 0.09	7.87	n.d.
10	23478-PeCDF	34.15	2940	0	0.0000	n.d.	0.02	n.d.
11	123478-HxCDF	40.89	1889	1096	0.5804	n.d. < 0.23	0.02	0.0213
12	123678-HxCDF	42.99	774	513	0.6630	0.21	0.02	0.0107
13	234678-HxCDF	42.99	915	513	0.5610	0.11	0.02	0.0119
14	123789-HxCDF	45.68	1326	364	0.2743	0.12	---	---
15	1234678-HpCDF	48.87	2422	2155	0.8898	---	0.01	0.0017
16	1234789-HpCDF	50.76	882	655	0.7425	0.17	10.30	n.d.
17	OCDF	54.04	2920	2982	1.0212	n.d.	0.03	0.0001
18	Overall_TEQ	0.00	17610	14445	0.8202	2.57	0.02	0.2457



RT: 23.05 - 54.80

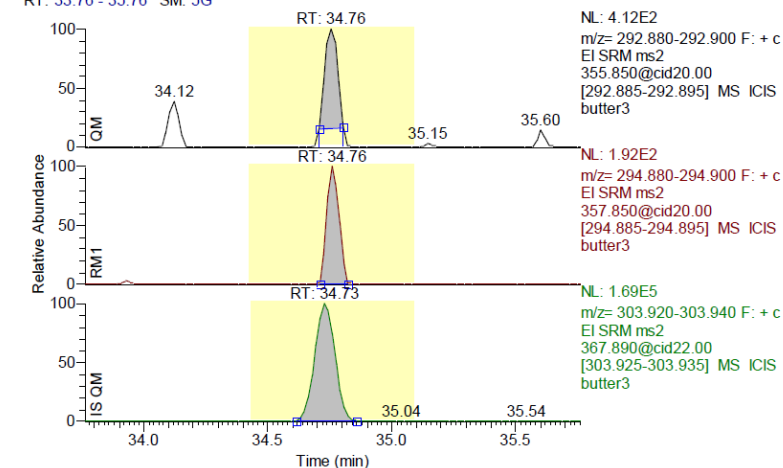


butter3_seq acquired 2015/10/16 09:57

SampleName: Id: 1 Comment:
Study: Client:

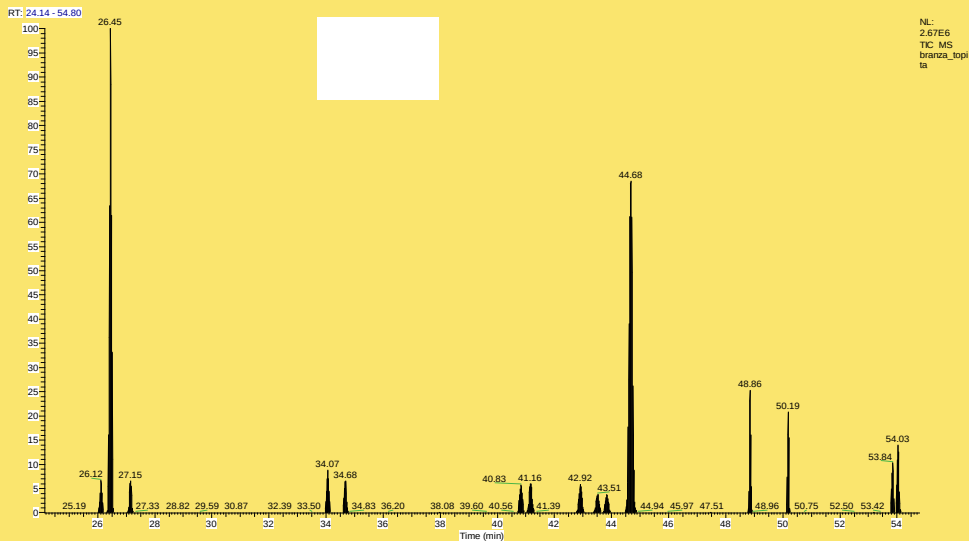
Chromatogram

RT: 33.76 - 35.76 SM: 5G



No.	Compound Name	QM Retention Time	QM Area	RM1 Area	RM1 Ratio (A)	Calculated Amount (A)	Detection Limit (A)	TEQ (A)
1	2378-TCDD	0.00	0	0	---	n.d.	0.03	n.d.
2	12378-PeCDD	34.71	107	253	2.3766	n.d. < 0.12	0.03	n.d.
3	123478-HxCDD	0.00	0	0	---	n.d.	0.11	n.d.
4	123678-HxCDD	0.00	0	0	---	n.d.	0.14	n.d.
5	123789-HxCDD	0.00	0	0	---	n.d.	0.13	n.d.
6	1234678-HpCDD	50.20	346	318	0.9183	0.09	0.02	0.0009
7	OCDD	0.00	0	6721	---	n.d.	0.10	n.d.
8	2378-TCDF	26.43	690	2828	4.1007	n.d.	0.04	n.d.
9	12378-PeCDF	32.47	147	194	1.3151	n.d. < 10.56	2.56	n.d.
10	23478-PeCDF	34.11	217	0	0.0000	n.d. < 0.05	0.02	n.d.
11	123478-HxCDF	40.91	183	278	1.5212	n.d. < 0.11	0.03	n.d.
12	123678-HxCDF	0.00	0	0	---	n.d.	0.03	n.d.
13	234678-HxCDF	0.00	0	0	---	n.d.	0.03	n.d.
14	123789-HxCDF	0.00	0	0	---	n.d.	2.84	n.d.
15	1234678-HpCDF	48.87	260	349	1.3405	n.d. < 0.07	0.01	n.d.
16	1234789-HpCDF	0.00	0	0	---	n.d.	4.45	n.d.
17	OCDF	54.06	466	872	1.8724	n.d. < 0.35	0.06	n.d.
18	Overall_TEQ	0.00	346	318	0.9183	0.09	0.02	0.0009

Brânză topită

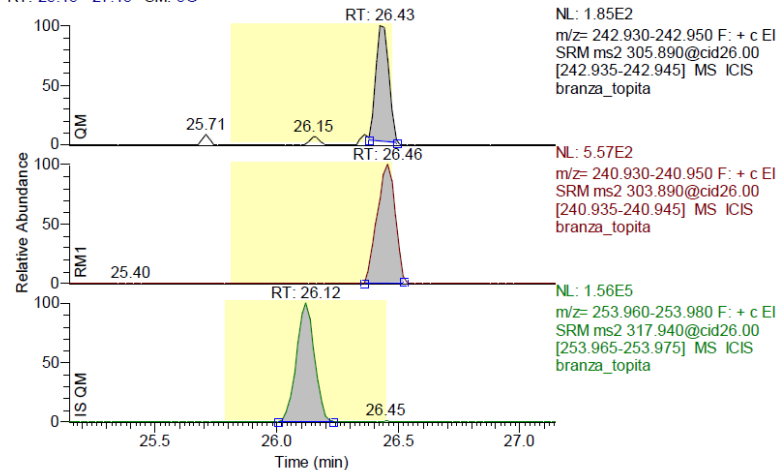


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SampleName: Id: 1 Comment:
Study: Client:

Chromatogram

RT: 25.15 - 27.15 SM: 5G



Performanțele sistemului GC-MS/MS TSQ 8000 Evo GC-MS/MS Thermo Scientific™

- Îndeplinește noile cerințe ale Regulamentului CE Nr. 589/2014 și Nr. 709/2014 ce permit utilizarea GC-MS/MS ca metodă de confirmare în analiza dioxinelor în probe de alimente și furaje
- Emite Rapoarte personalizate care combină rezultatele din analiza de dioxine și PCB similare dioxinelor și efectuează automat calculele complexe cerute de regulamentele UE
- Realizează o înaltă eficiență a sursei ionice EI (limită de detecție instrumentală: 0.5 fg)
- Permite o analiză cromatografică de mare performanță și productivitate (scurtarea timpului de analiză, conservarea resurselor).



Vă mulțumesc pentru atenție!

Această lucrare a fost posibilă prin sprijinul financiar oferit prin Programul Operational Sectorial "Creșterea Competitivității Economice" , co-finantat prin Fondul European de Dezvoltare Regională, "Investiții pentru viitorul dumneavoastră, în cadrul proiectului POSCCE Axa II, Operatiunea: O2.2.1-2013, ID nr.1887/Cod SMIS-CSNR: 49164 INOVA-OPTIMA

