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DFS

High Resolution Sector Field MS

Optimization of Analytical Conditions for Improved Sensitivity in the Analysis of Deca-BDE on a DFS High Resolution GC/HRMS system

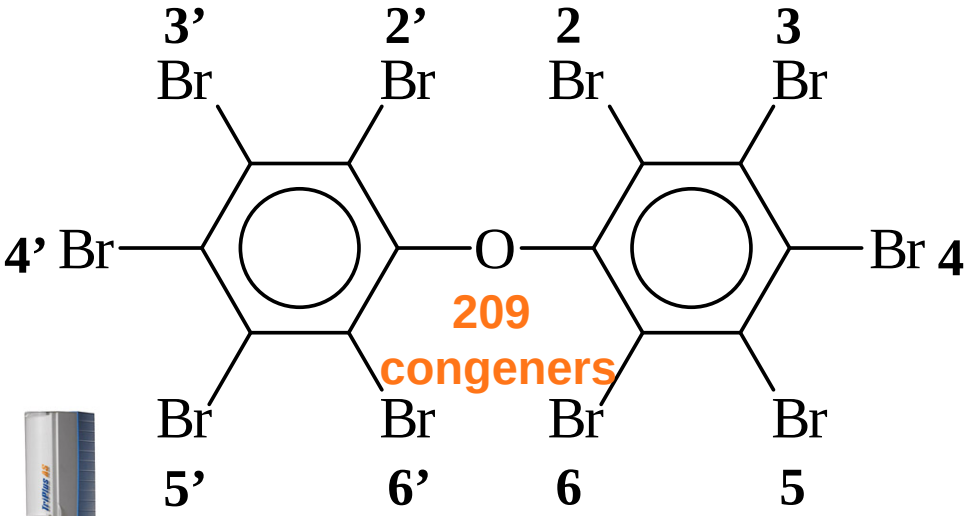
Dirk Krumwiede

Presentation Overview
Analysis of **poly**ly**br**ominated **Di**ph**e**nyl**e**thers (PBDE)

1.) Analysis of PBDE
– special aspects and requirements

2.) Parameter optimization for the analysis of the Deca–BDE using SSL and PTV injectors

3.) A dual column setup
combining highest sensitivity for Deca–BDE and good separation efficiency for all other congeners



Part 1: Analysis of PBDE
What is special with PBDE analysis ?

- M^+ peaks are not the most intense ions for all bromination degrees

- A high mass range has to be covered: (m/z 248 to 799)

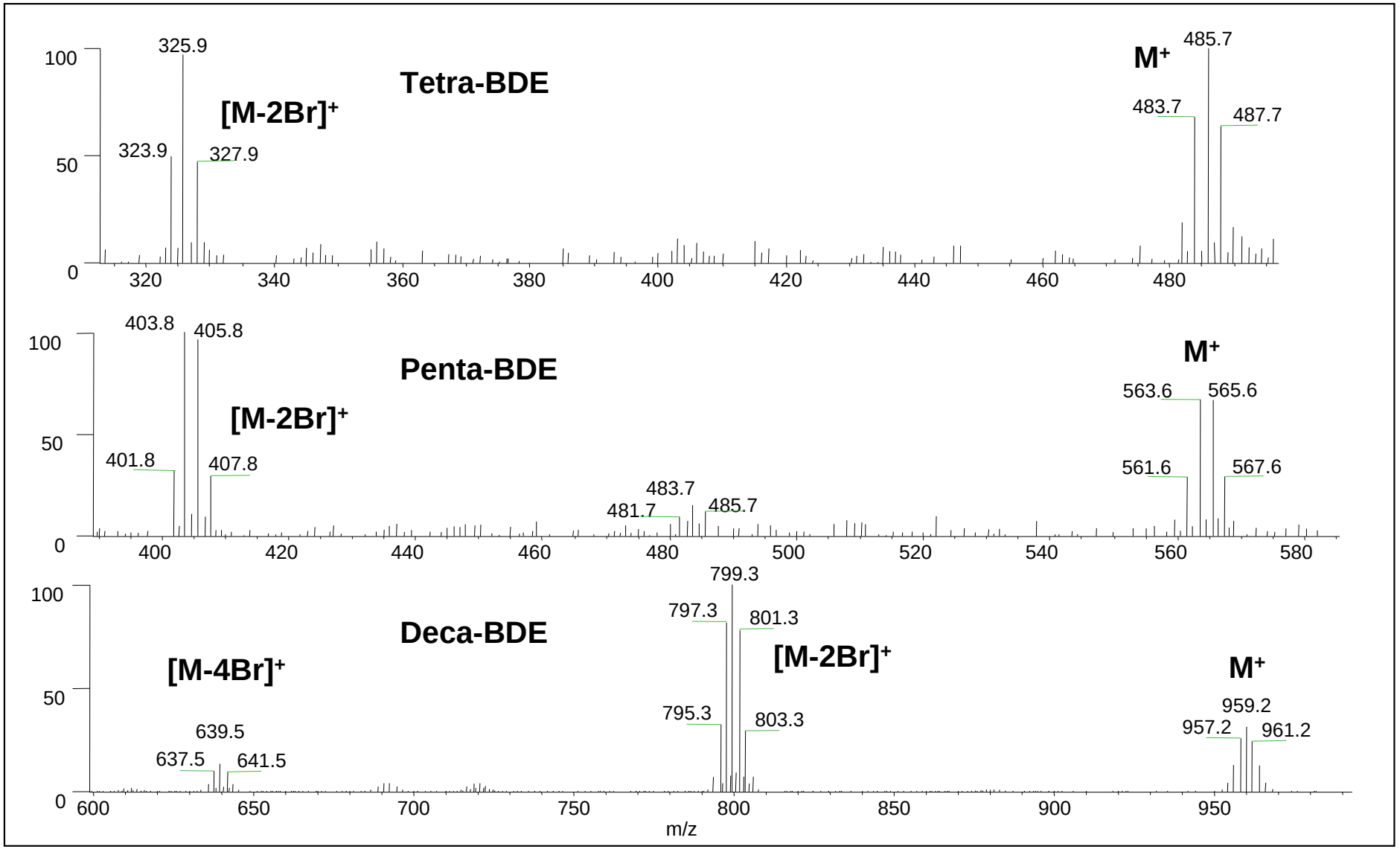
- **large electric jumps for window defining runs**
- **finding suitable reference masses for the high mass range**

- adaptation of temperatures for the high boiling PBDE:

Injector, oven, transfer line and ion source temperatures

- Deca–BDE is thermolabile and high boiling

Full scan results
comparing M^+ and $[M-2Br]^+$ isotope peak intensities

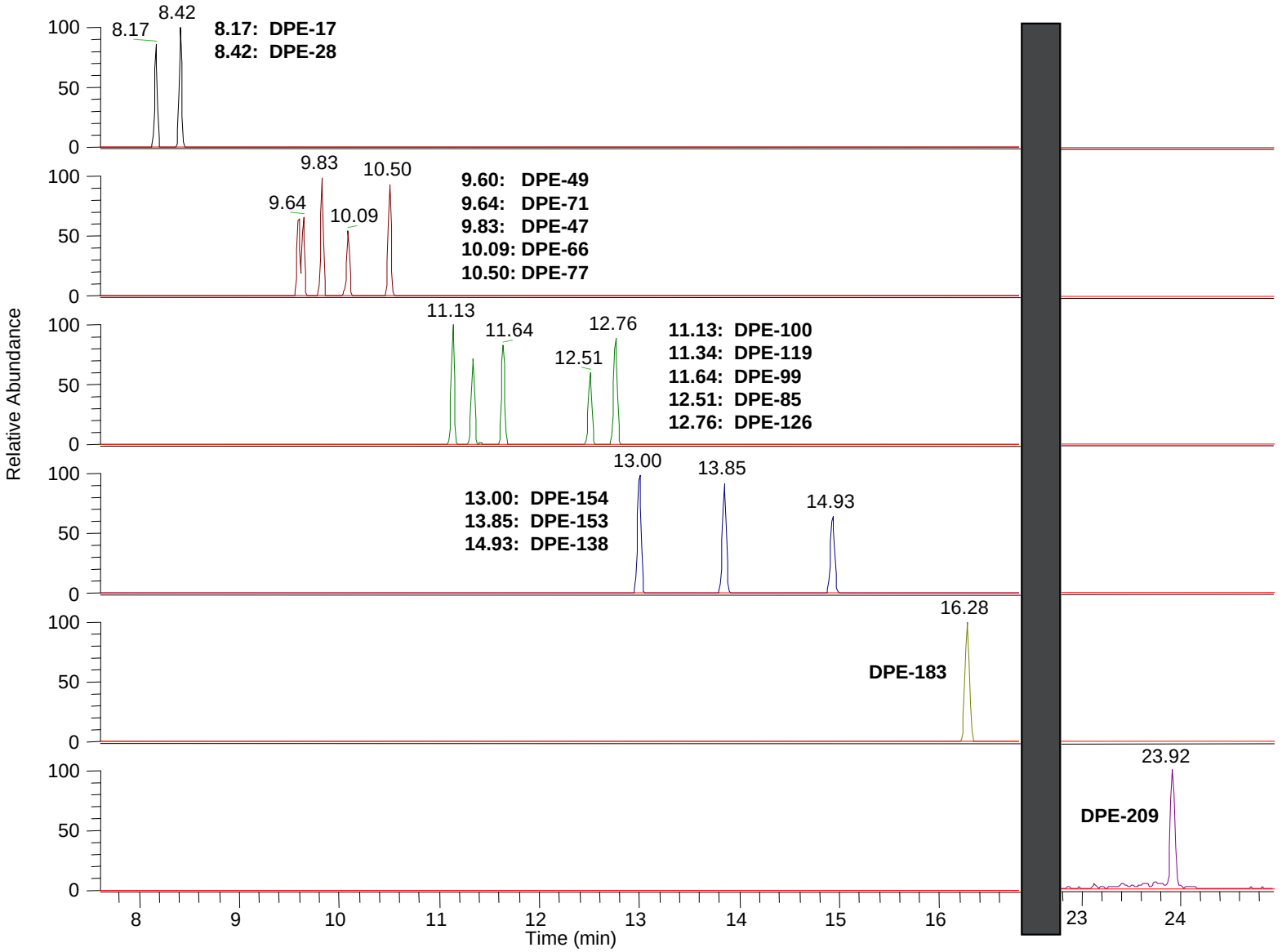


Mass/Intensity List for PBDE

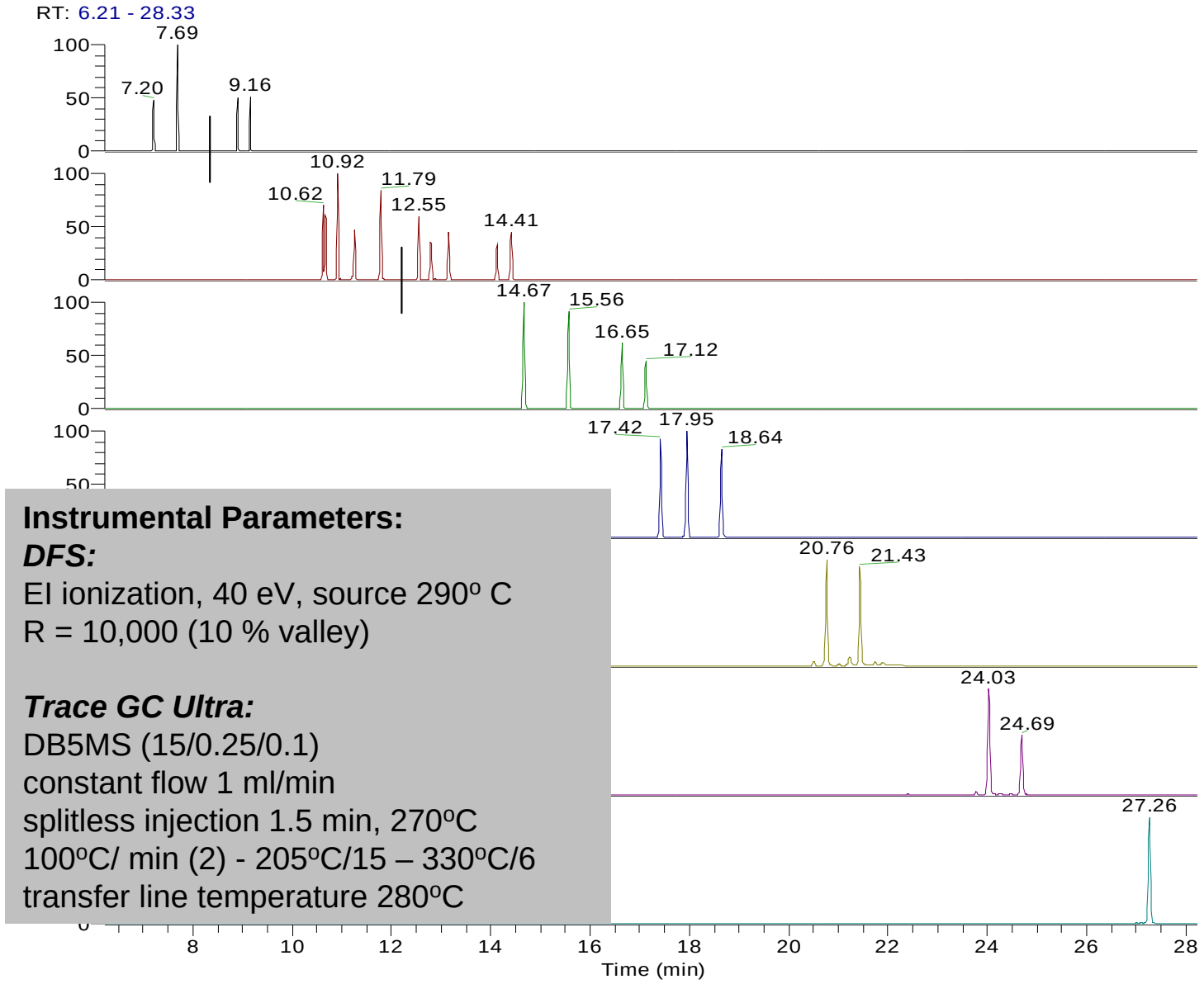
relative intensities of M^+ versus $[M-2Br]^+$

	# Br	m		m+2		m+4		m+6		m+8		m+10		m+12		Int. M/M-2Br
$[M]^+$	1	247,984	*100*	249,982	*98*											**100**
	2	325,894	*51*	327,892	*100*	329,890	*49*									**100**
	3	403,805	*34*	405,803	*100*	407,801	*97*									**100**
	4			483,713	*68*	485,711	*100*	487,709	*65*							**100**
	5			561,624	*51*	563,622	*100*	565,620	*97*							**85**
	6					641,532	*76*	643,530	*100*	645,528	*73*					**60**
	7					719,443	*61*	721,441	*100*	723,439	*97*					**55**
	8							799,351	*81*	801,349	*100*	803,347	*78*			**50**
	9							877,262	*68*	879,260	*100*	881,258	*97*			**40**
	10									957,171	*85*	959,168	*100*	961,166	*81*	**25**
$[M-2Br]^+$	1															**0**
	2															**0**
	3															**0**
	4	323,879	*51*	325,877	*100*	327,875	*49*									**95**
	5	401,789	*34*	403,787	*100*	405,785	*97*									**100**
	6			481,698	*68*	483,696	*100*	485,694	*65*							**100**
	7			559,608	*51*	561,606	*100*	563,604	*97*							**100**
	8					639,517	*76*	641,515	*100*	643,513	*73*					**100**
	9					717,427	*61*	719,425	*100*	721,423	*97*					**100**
	10							797,336	*81*	799,333	*100*	801,331	*78*			**100**

Mass Chromatogram of a 6 window run
Separation by bromination degree on a 15 m column



CS3-E: BDE 2-10 brominated on 15 m column / SSL inj.



2-BDE / 3-BDE

4-BDE / 5-BDE

6-BDE

7-BDE

8-BDE

9-BDE

10-BDE

Instrumental Parameters:

DFS:

EI ionization, 40 eV, source 290° C

R = 10,000 (10 % valley)

Trace GC Ultra:

DB5MS (15/0.25/0.1)

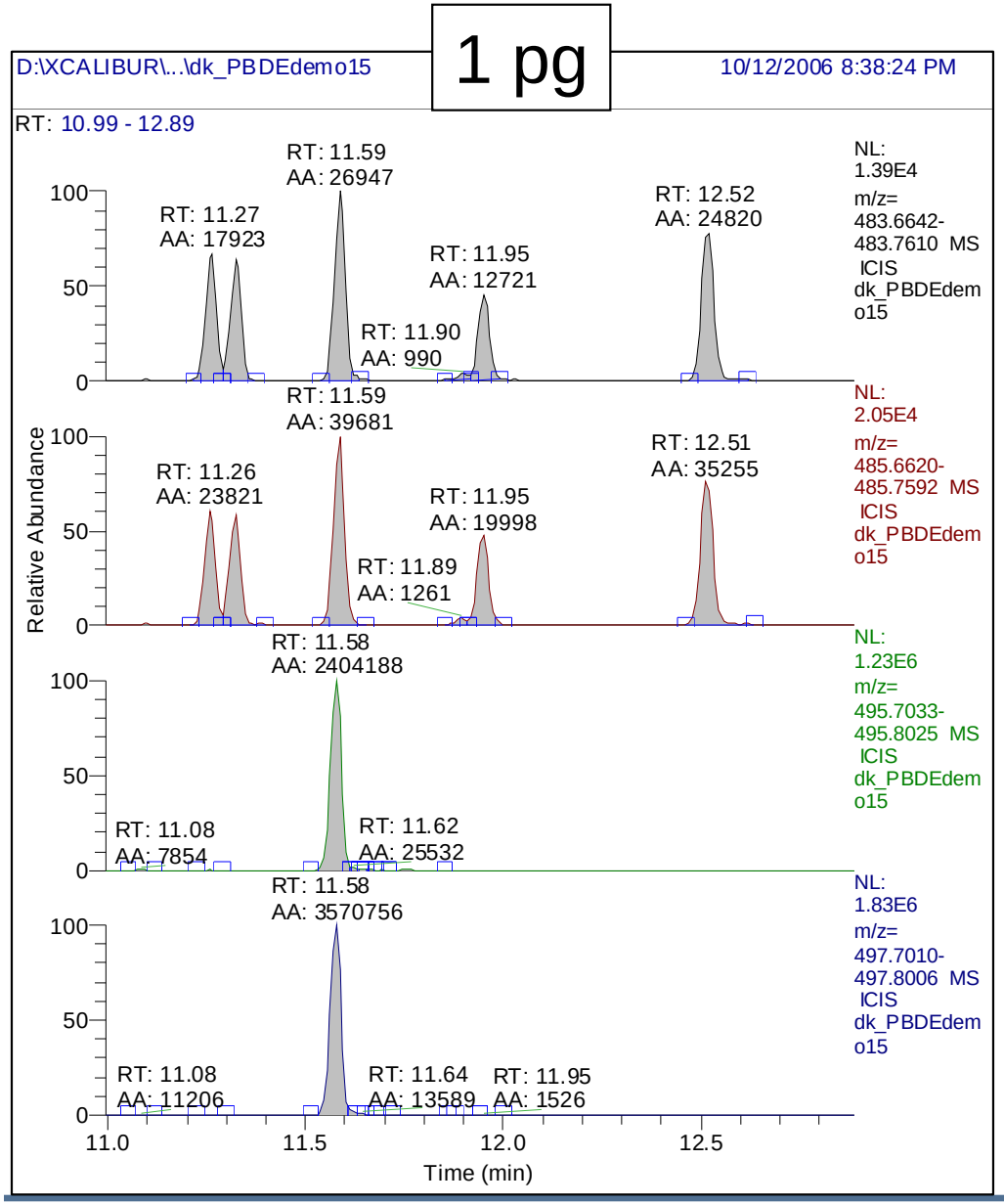
constant flow 1 ml/min

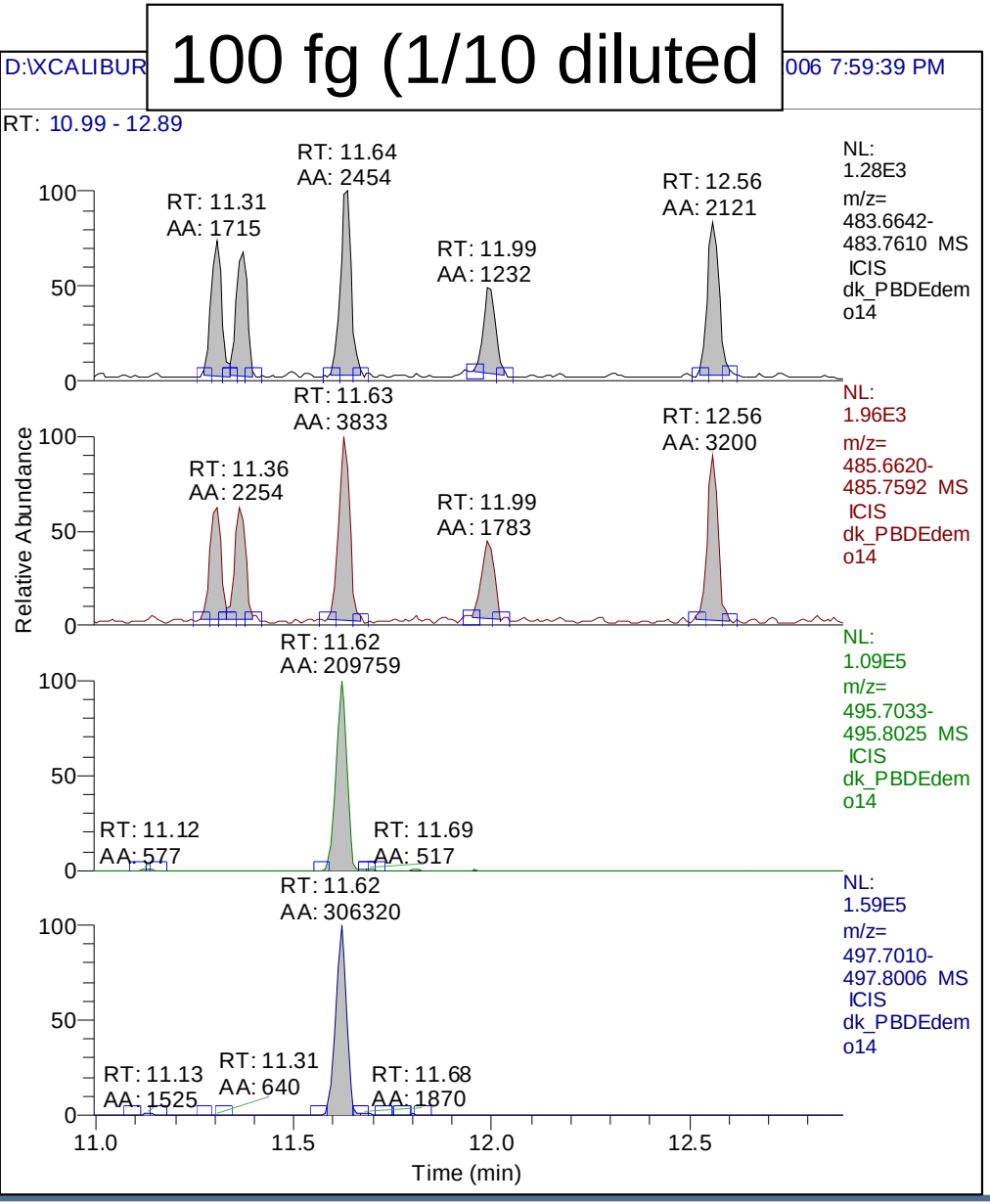
splitless injection 1.5 min, 270°C

100°C/ min (2) - 205°C/15 – 330°C/6

transfer line temperature 280°C

CS3-E: BDE tetra separation on 15 m column / SSL inj.





DFS – PBDE analysis in low fg range (like PCB, dioxin/furans)
Application Notes on PBDE

Application Note: 30098

DFS - Analysis of Brominated Flame Retardants with High Resolution GC/MS

Dirk Kramwiede, Hans-Joachim Hübschmann, Thermo

Key Words

- Flame Retardants (PBDE)
- HRGC / HRMS
- Multiple Ion Detection (MID)
- Persistant Organic Pollutants (POPs)
- RoHS / WEEE

Introduction

Polybrominated diphenyl ethers (PBDEs) are among most important and widely used flame retardants in variety of different industrial products. They are fo worldwide in matrices, moving them into the focus recent legislation banning certain PBDE congeners[1] directive 2003/11/EC prohibits the use of Penta-BD Octa-BDE for the member states of the European community[2].

As a result analysis of PBDEs have received inc interest due to their known toxicity. Similar to dioxins/furans and PCB's (polychlorinated biphenyl polybrominated diphenyl ethers exist in a higher nu of congeners (209) (Figure 1).

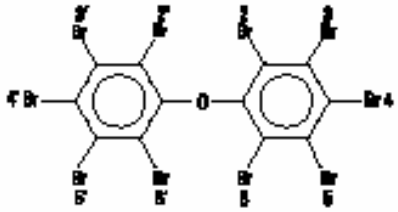
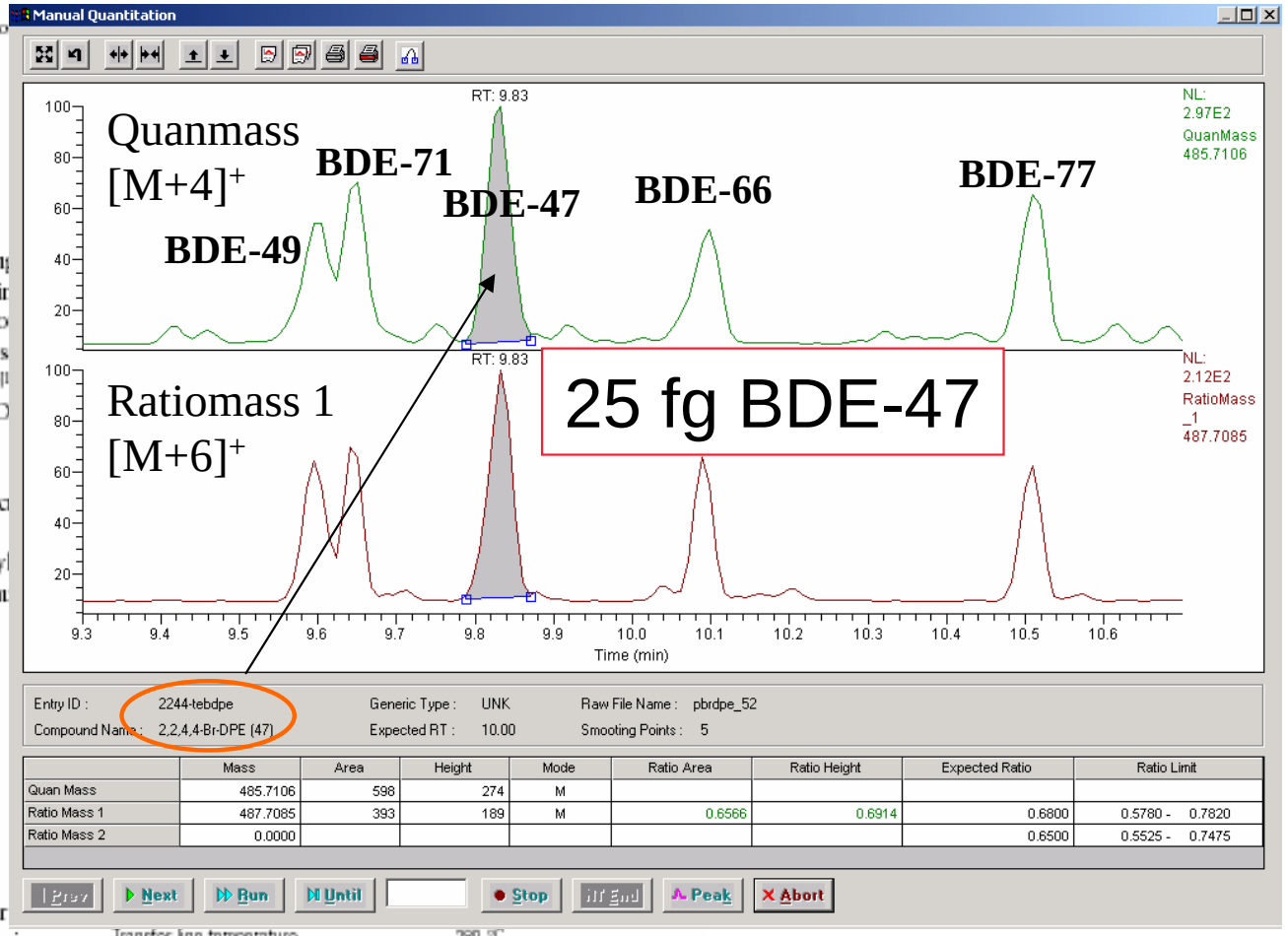


Figure 1: PBDE chemical structure, here Deca-BDE

The most efficient analysis technique by far for three application areas is high resolution GC/MS using isotope dilution technique for quantitation with highest precision and significance.



Transfer line temperature 280 °C

Table 1: GC parameters

Part 2: Optimized analysis for Deca–BDE
using SSL and PTV injectors

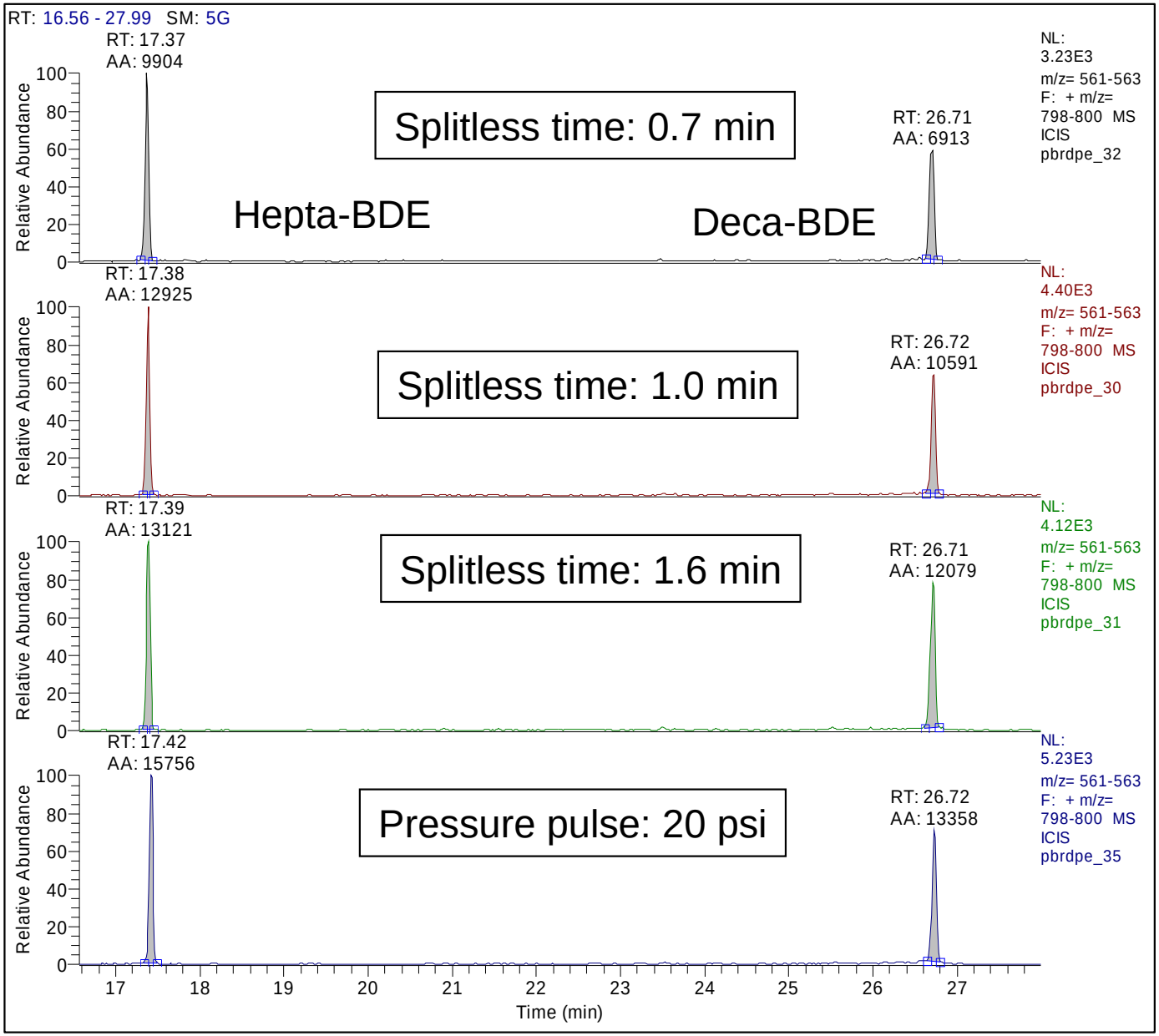
Parameters influencing sensitivity for Deca–BDE:

- liner type and diameter
- injector type SSL ↔ PTV
- pressure pulse / surge
- splitless time

- oven program
- column length
- column flow

- source temperature
- ionization energy (eV)

SSL injector: splitless time and pressure pulse

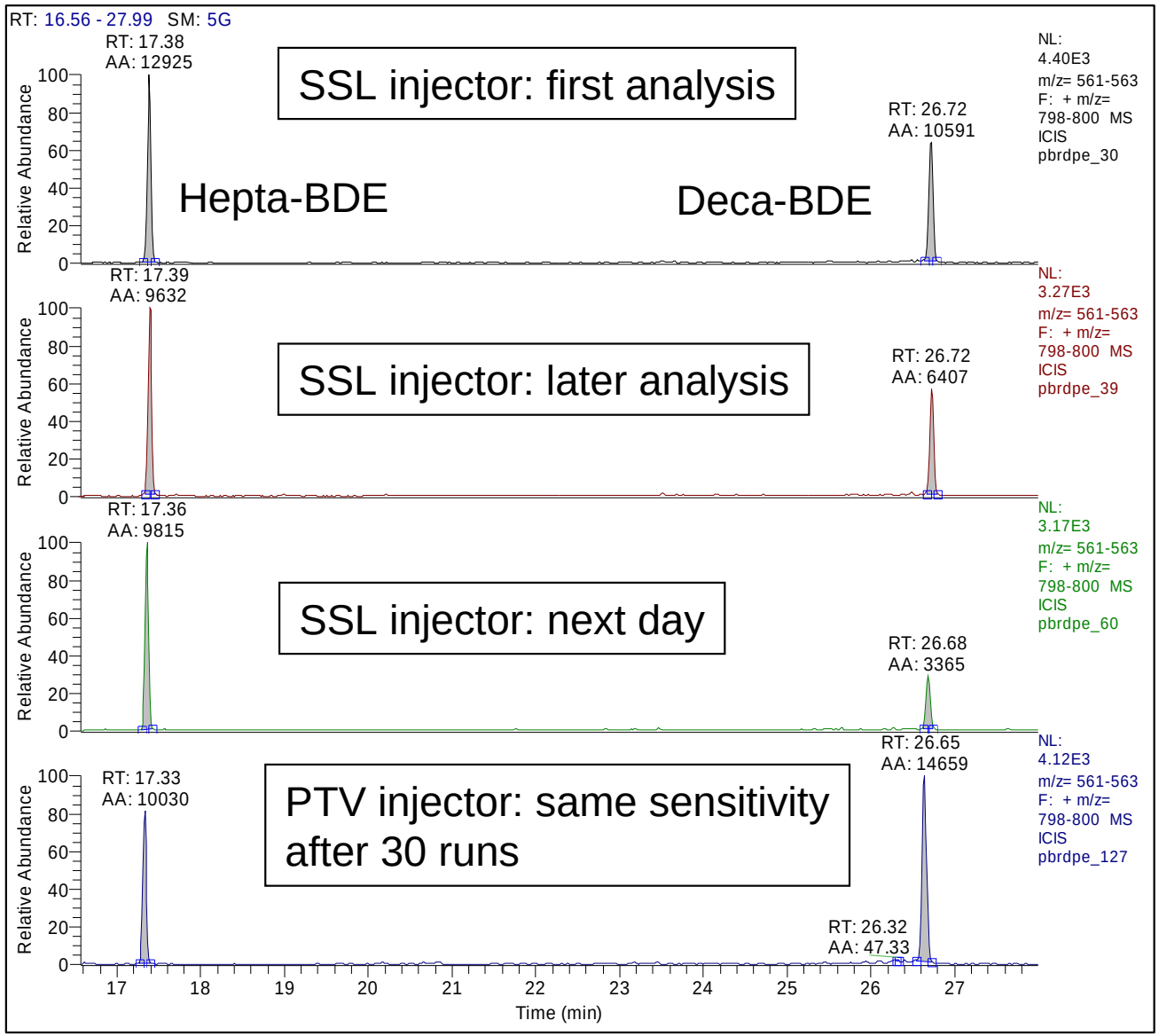


DB5 15 m; 0.25mm;
0.1 um film, 1 ml/min He

SSL injector with
5 mm I.D. liner

➔ Too low splitless time causes significant loss of intensity for Deca-BDE.

SSL or PTV for Deca-BDE analysis ?
Decrease of sensitivity over time



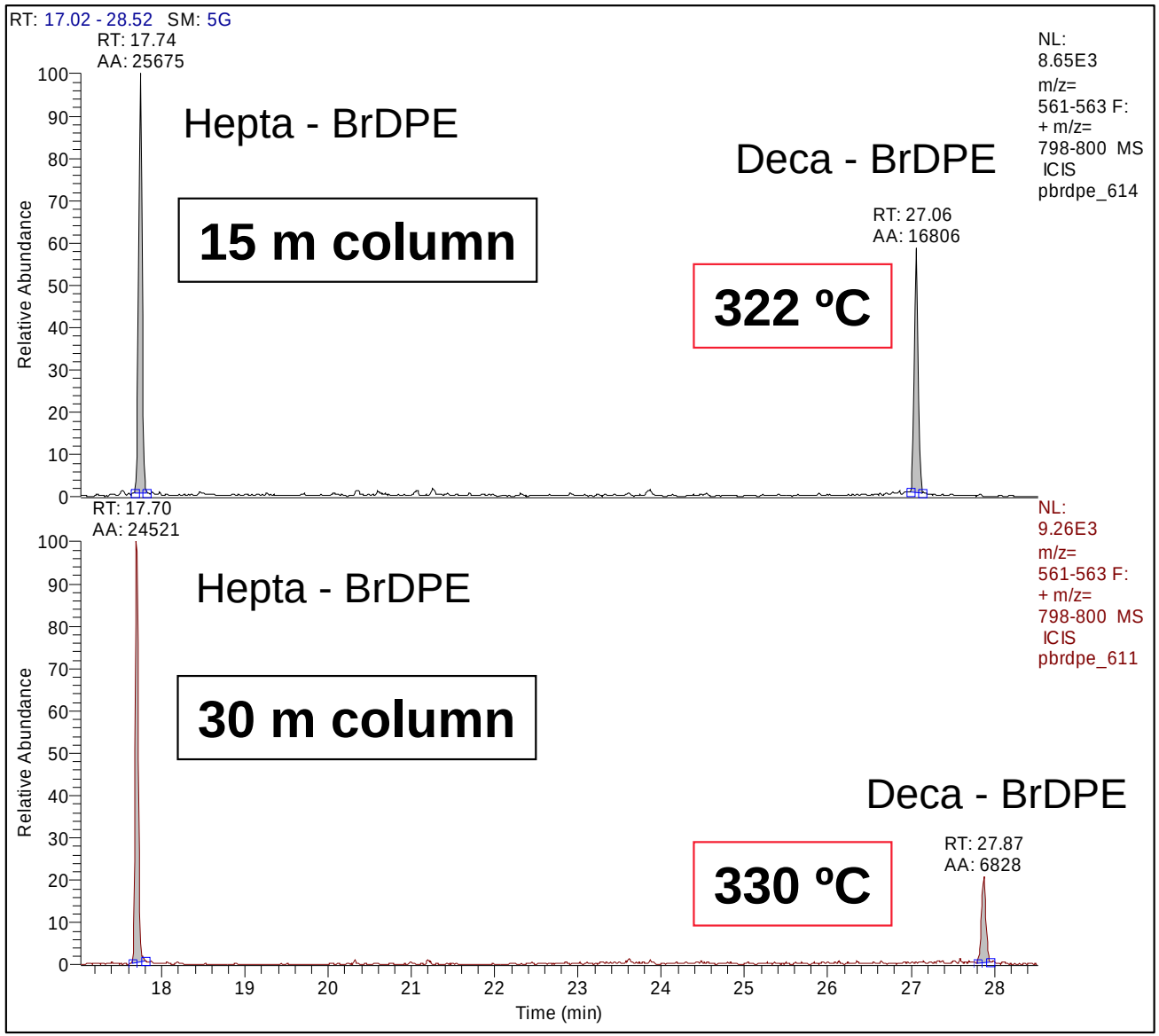
DB5 15 m; 0.25mm;
0.1 um film, 1 ml/min He

SSL injector with
5 mm I.D. liner

PTV injector with 2 mm
I.D. metal liner

➔ PTV offers better sensitivity and stability for Deca - BDE analysis.

Column length and Deca–BDE response



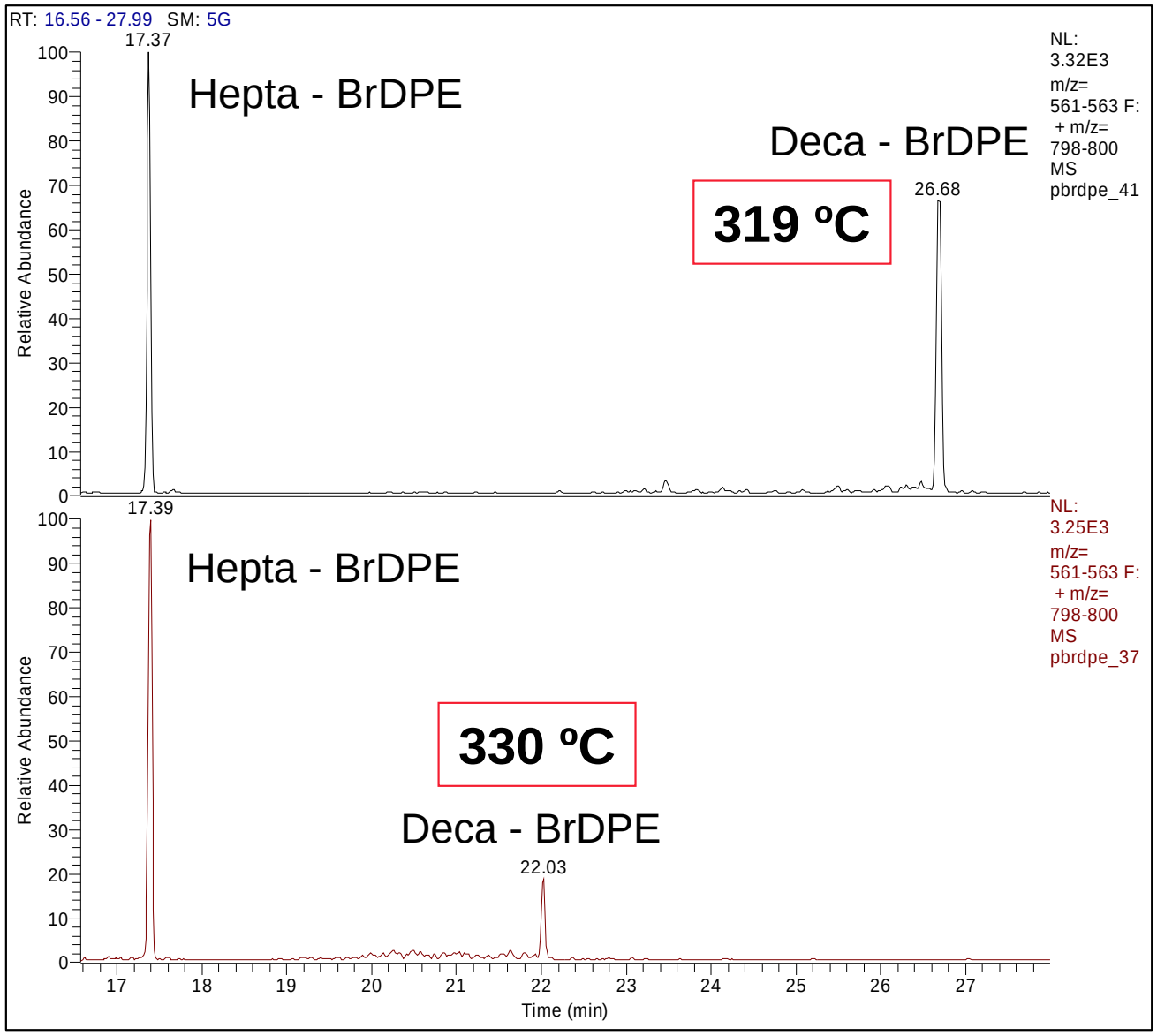
DB5 15 m / 30 m; 0.25mm;
0.1 um film;
Flow: 0.8 ml/min He

120 °C (2 min) –
15 °C/min -> 205 °C
- 6 °C/min -> 330 °C

120 °C (2 min) –
20 °C/min -> 230 °C
-6 °C/min -> 330 °C

Oven program and Deca–BDE response

same 15 m column / two different oven programs

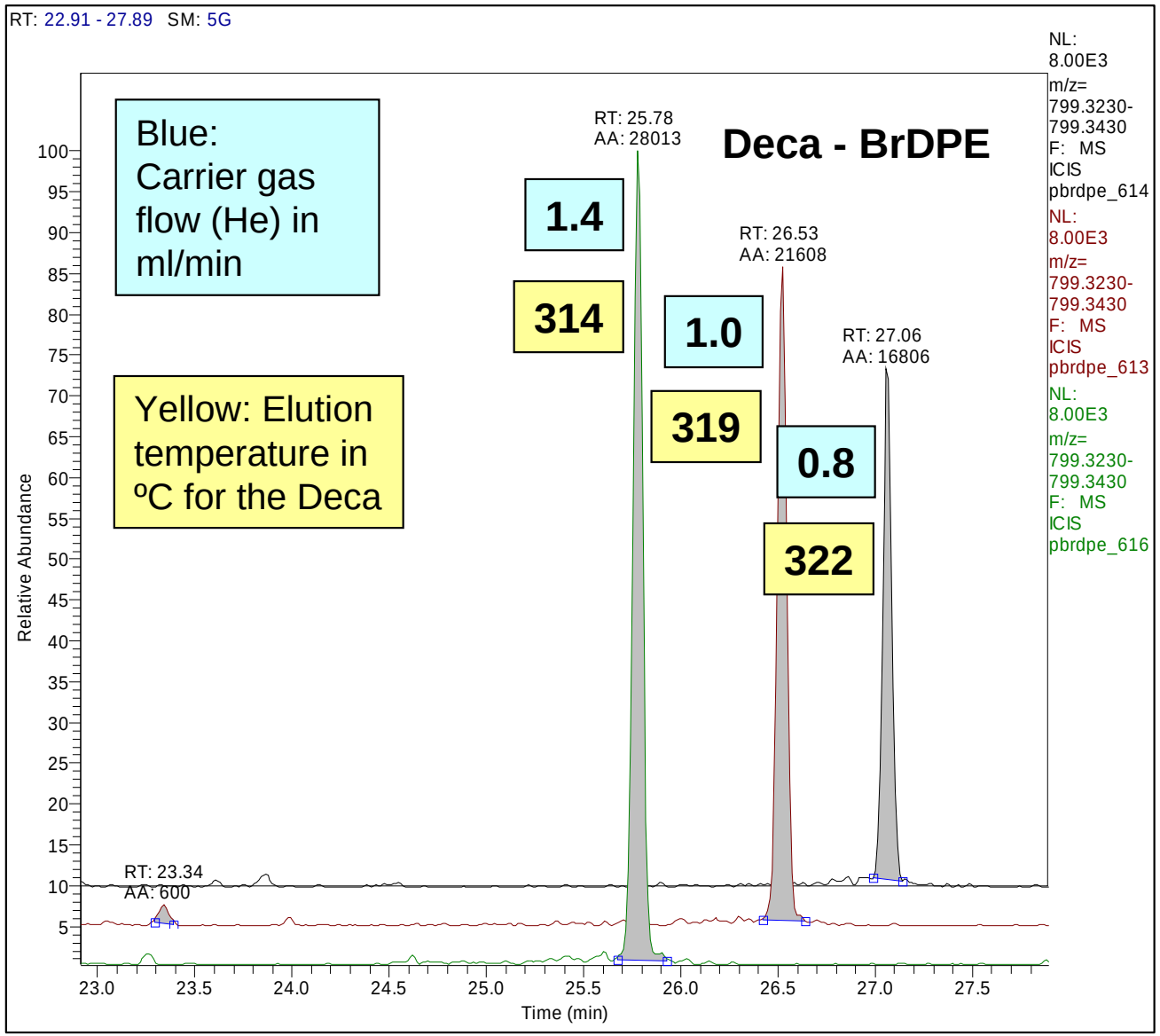


DB5 15 m; 0.25mm;
0.1 um film; 1 ml/min He

120 °C (2 min) –
15 °C/min -> 205 °C
- **6 °C/min** -> 330 °C

120 °C (2 min) –
15 °C/min -> 205 °C
-6 °C/min -> 268 °C
- **40 °C/min** -> 330 °C

Carrier gas flow and Deca–BDE response

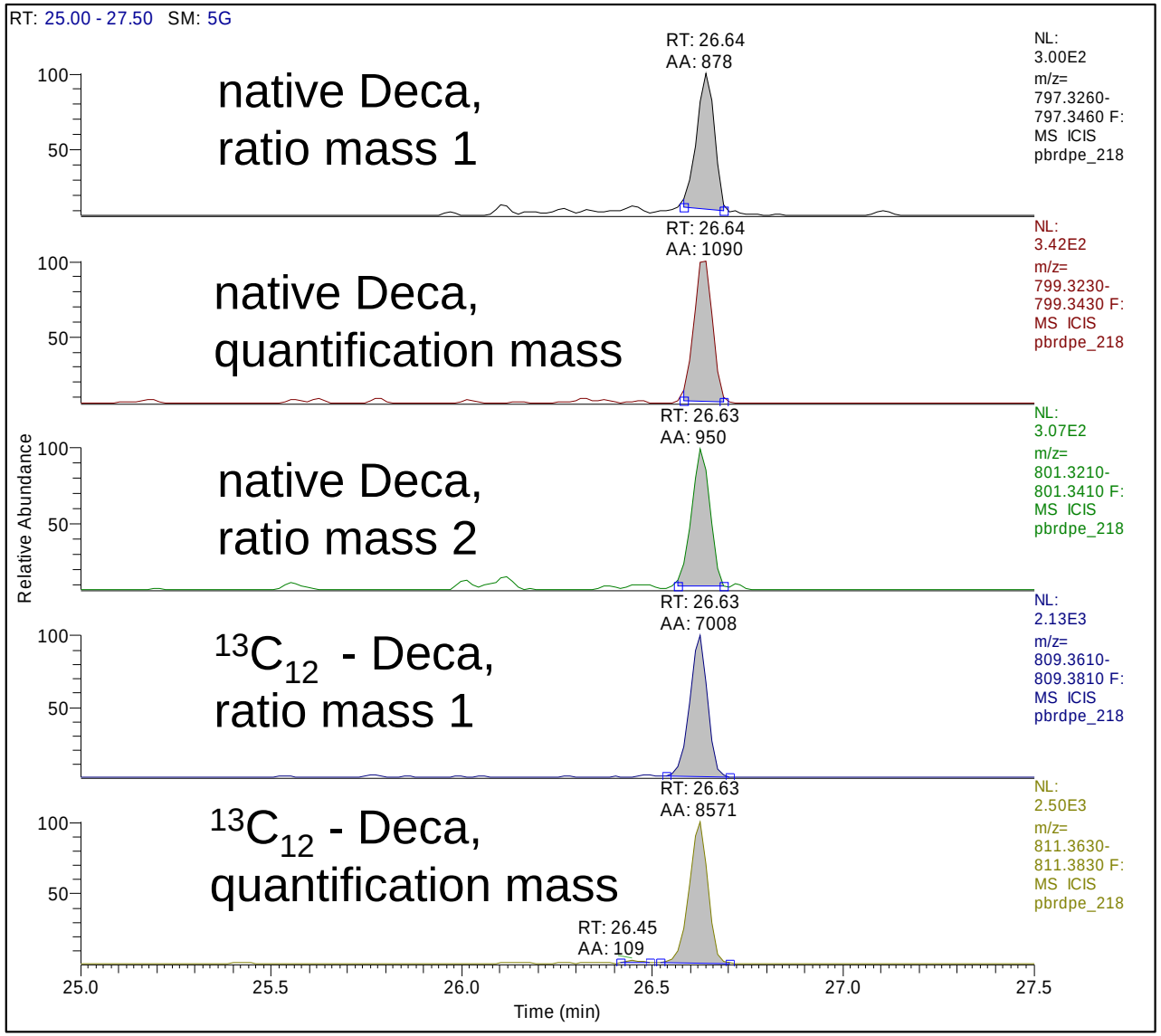


DB5 15 m; 0.25mm; 0.1 um film

Oven program:
120 °C (2 min) –
15 °C/min -> 205 °C
- 6 °C/min -> 330 °C

➔ Nearly a factor 2 between low and high flow setting.

Deca – BDE optimized sensitivity on a 15 m DB5
1 pg Deca (1 ul 1:10 diluted CS1 standard)



DB5 15 m; 0.25mm;
0.1 um film, 1 ml/min He

PTV injector:
Glas liner 1 mm I.D.;
120 ºC (0.2) – 8 ºC/min –
320 ºC; 1 min splitless

Oven:
120 °C (2 min) –
15 °C/min -> 205 °C
- 6 °C/min -> 330 °C

Source / transfer line:
280 °C

Lock / Cali mass (PFK):
754.95; 766.95

Optimized analysis for Deca–BDE
using SSL and PTV injectors - conclusions

Parameters influencing sensitivity for Deca–BDE:

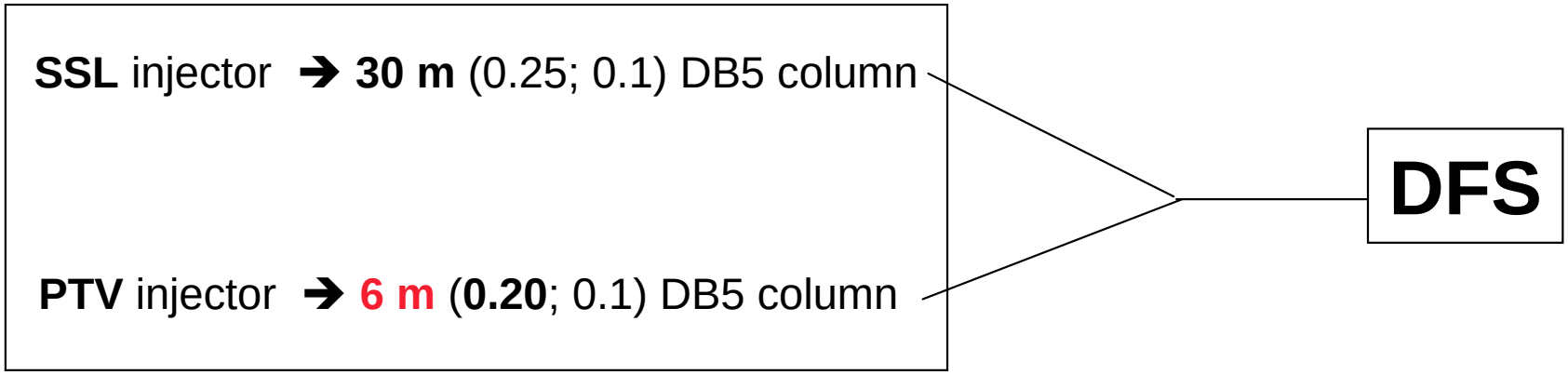
- liner type and diameter - injector type SSL ↔ PTV - pressure pulse / surge - splitless time	➔ No significant difference from liner I.D. ➔ PTV is preferable for Deca-BDE. ➔ Pressure pulse useful for SSL / PTV ➔ Assure sufficient splitless time
- oven program - column length - column flow	➔ Rule of thumb: Elution temperature for Deca-BDE should be as low as possible
- source temperature - ionization energy (eV)	➔ 270 – 280 ºC ➔ same as for dioxins (35 / 40 eV)

Part 3: A dual column setup for PBDE analysis
combining sensitivity and separation efficiency

Following some minor adaptations of source and transferline parts two columns were installed into the same GC (two injectors) and source using a Y-shaped dual column adaptor.

This setup allows to inject from the same vial in subsequent runs on two different columns.

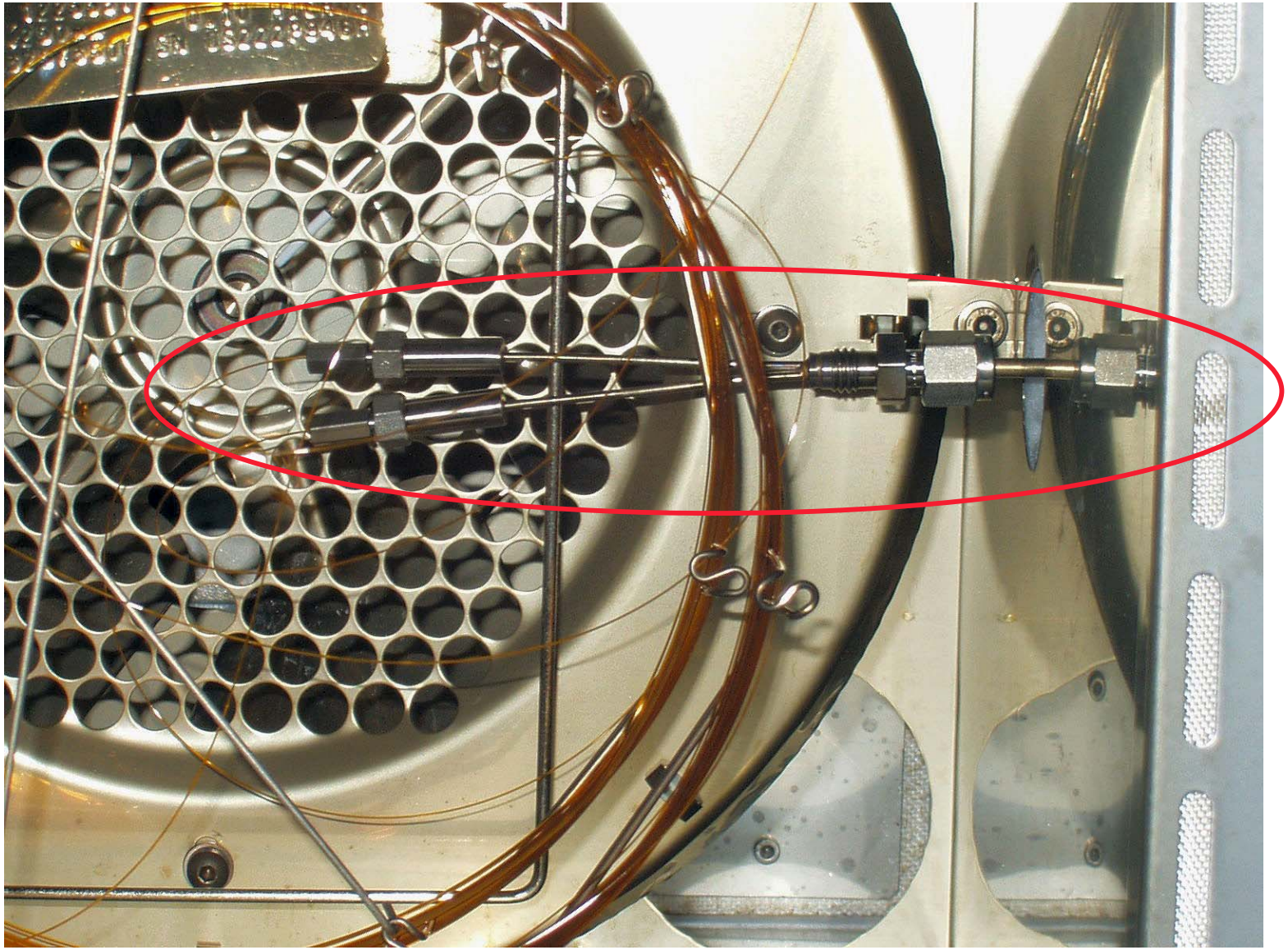
For PBDE:



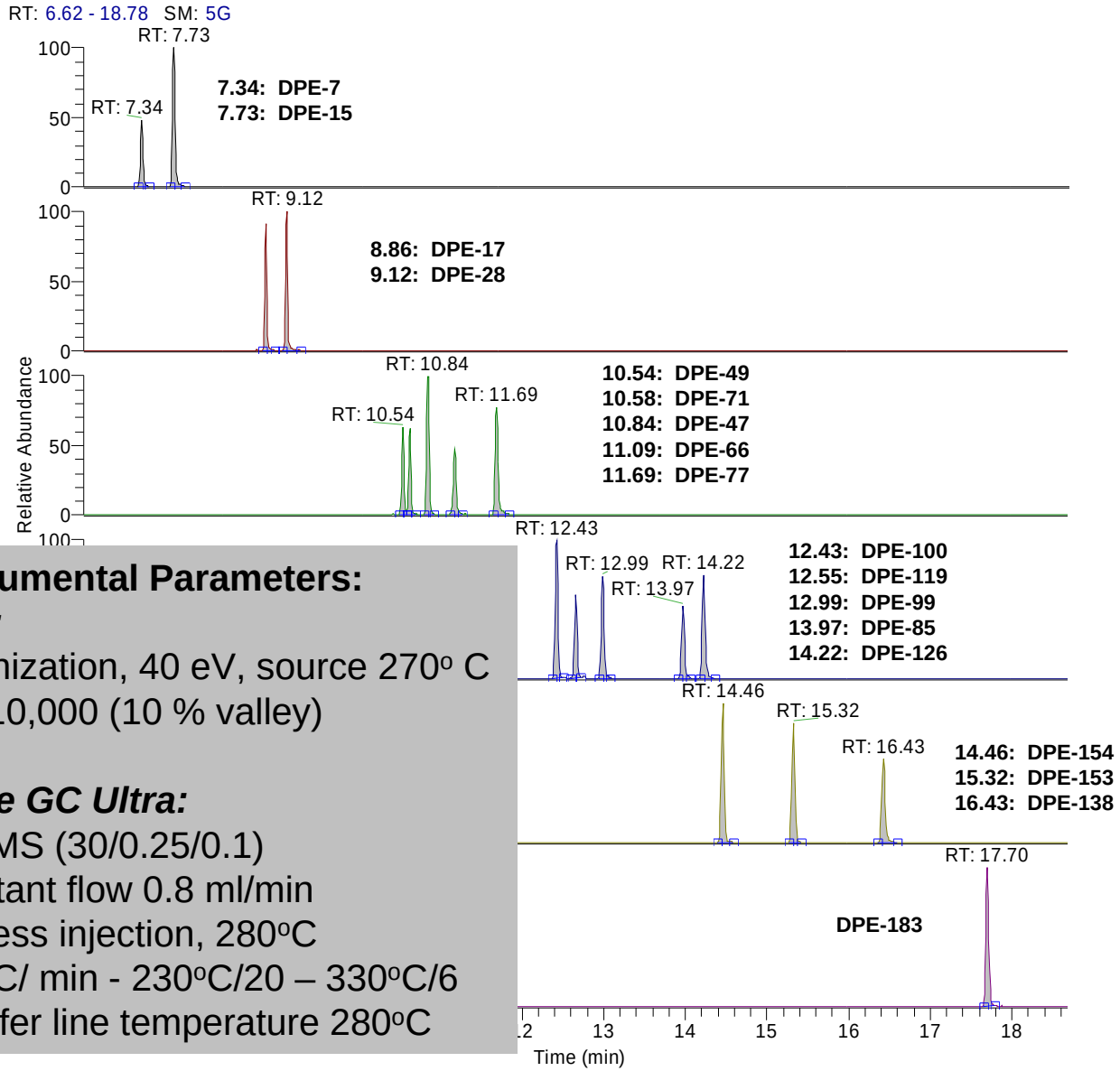
Trace GC (dual injector)

Transfer line with
2 column adaptor

Dual column setup for PBDE analysis



Typical chromatogram
Separation on DB5 (here 30 m) by bromination degree



Instrumental Parameters:
DFS*:*
EI ionization, 40 eV, source 270° C
R = 10,000 (10 % valley)

Trace GC Ultra:
DB5MS (30/0.25/0.1)
constant flow 0.8 ml/min
splitless injection, 280°C
120°C/ min - 230°C/20 – 330°C/6
transfer line temperature 280°C

Di-BDE
327.892

Tri-BDE
405.803

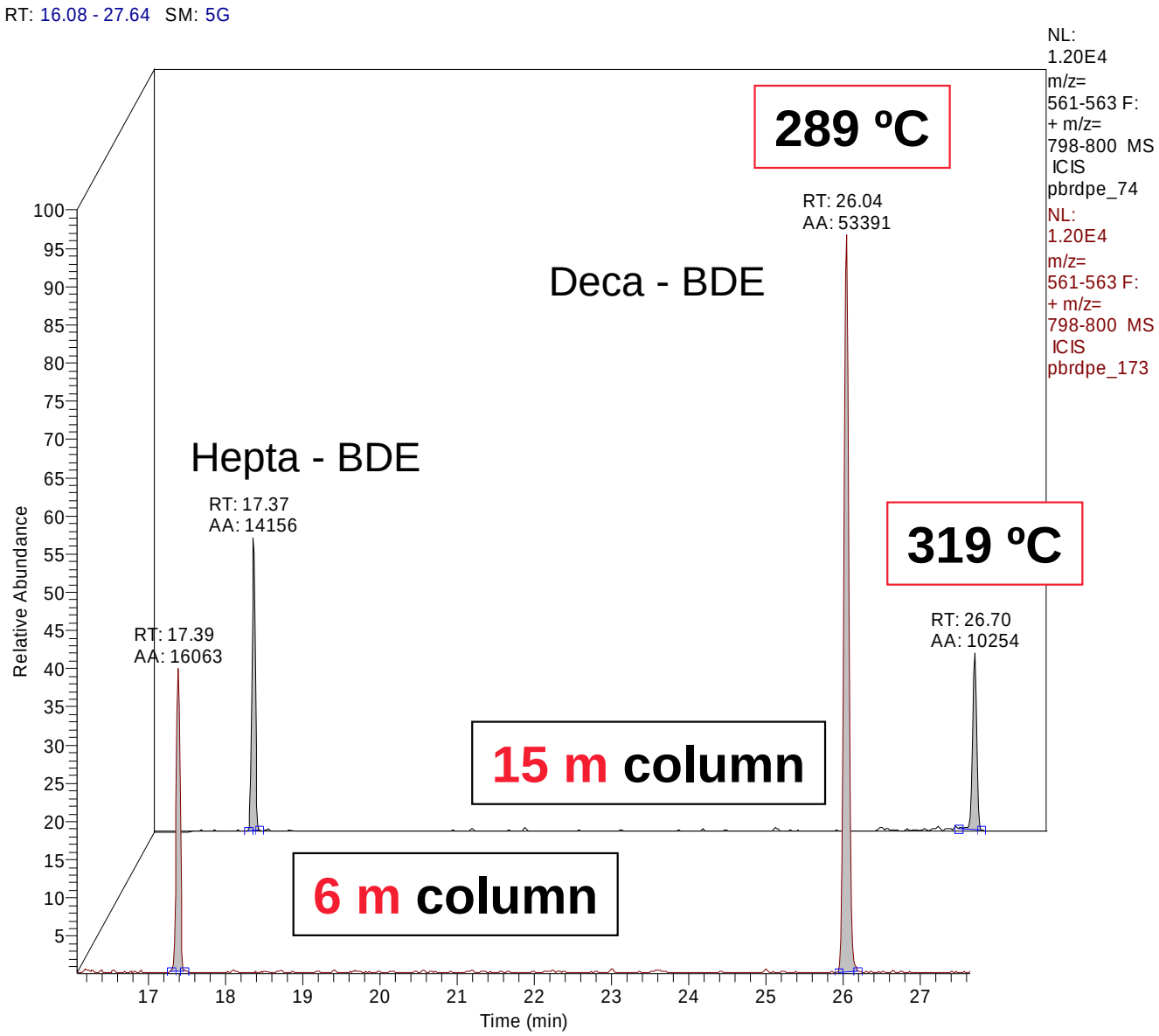
Tetra-BDE
485.711

Penta-BDE
563.622

Hexa-BDE
483.696

Hepta-BDE
561.606

Deca–BDE response on 15m / 6m column
(15m – single column / 6 m – dual column setup)

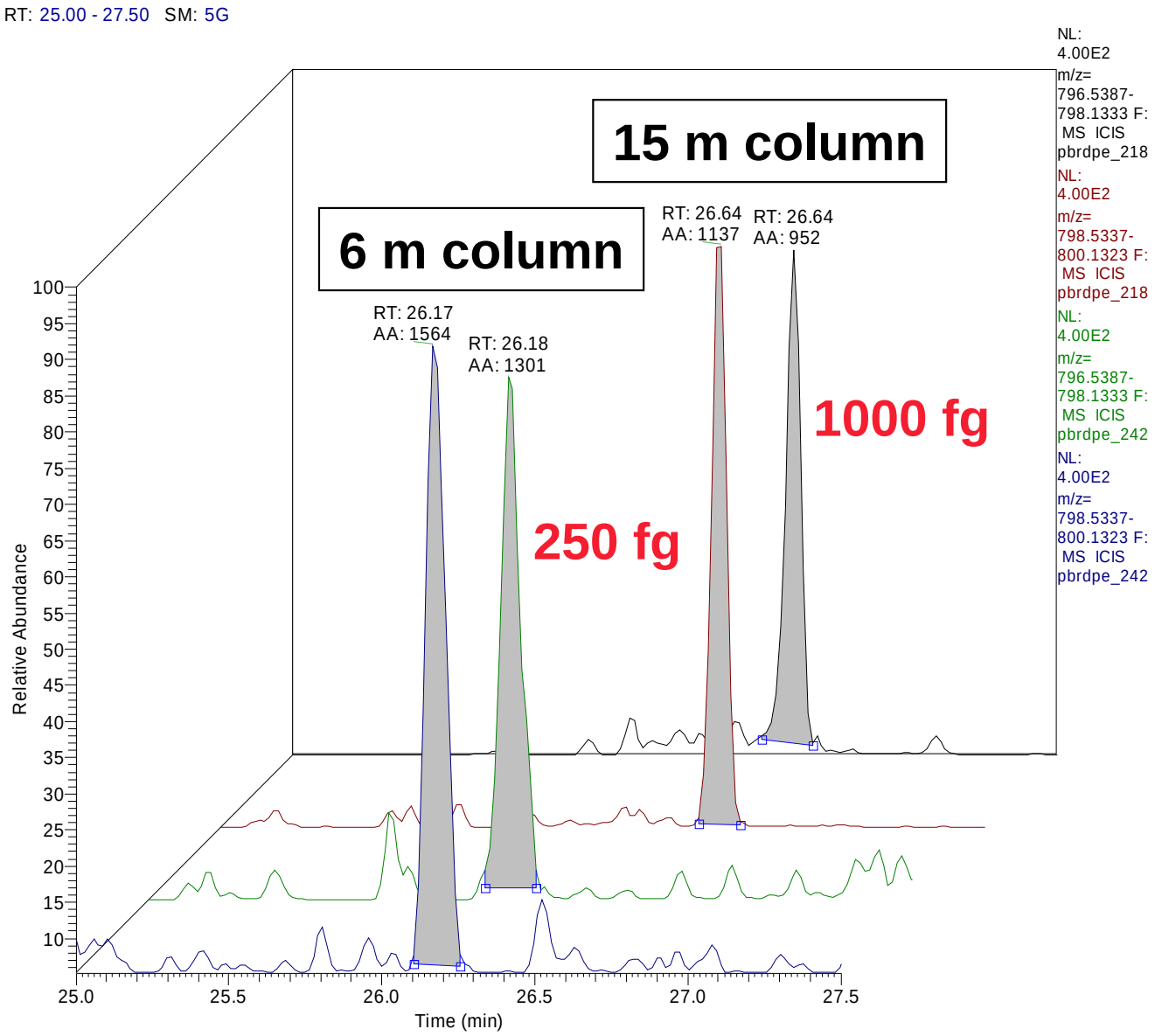


DB5 15 m; 0.25mm; 0.1 um
DB5 6 m; 0.2mm; 0.1 um

120 °C (2 min) –
15 °C/min -> 205 °C
-6 °C/min
-> 330 °C (15 m)
-> 305 °C (6 m)

For display:
4.48 min offset on Ret. Times of 6 m Chromatogram

Deca–BDE response on 15m / 6m column
(15m – single column / 6 m – dual column setup)

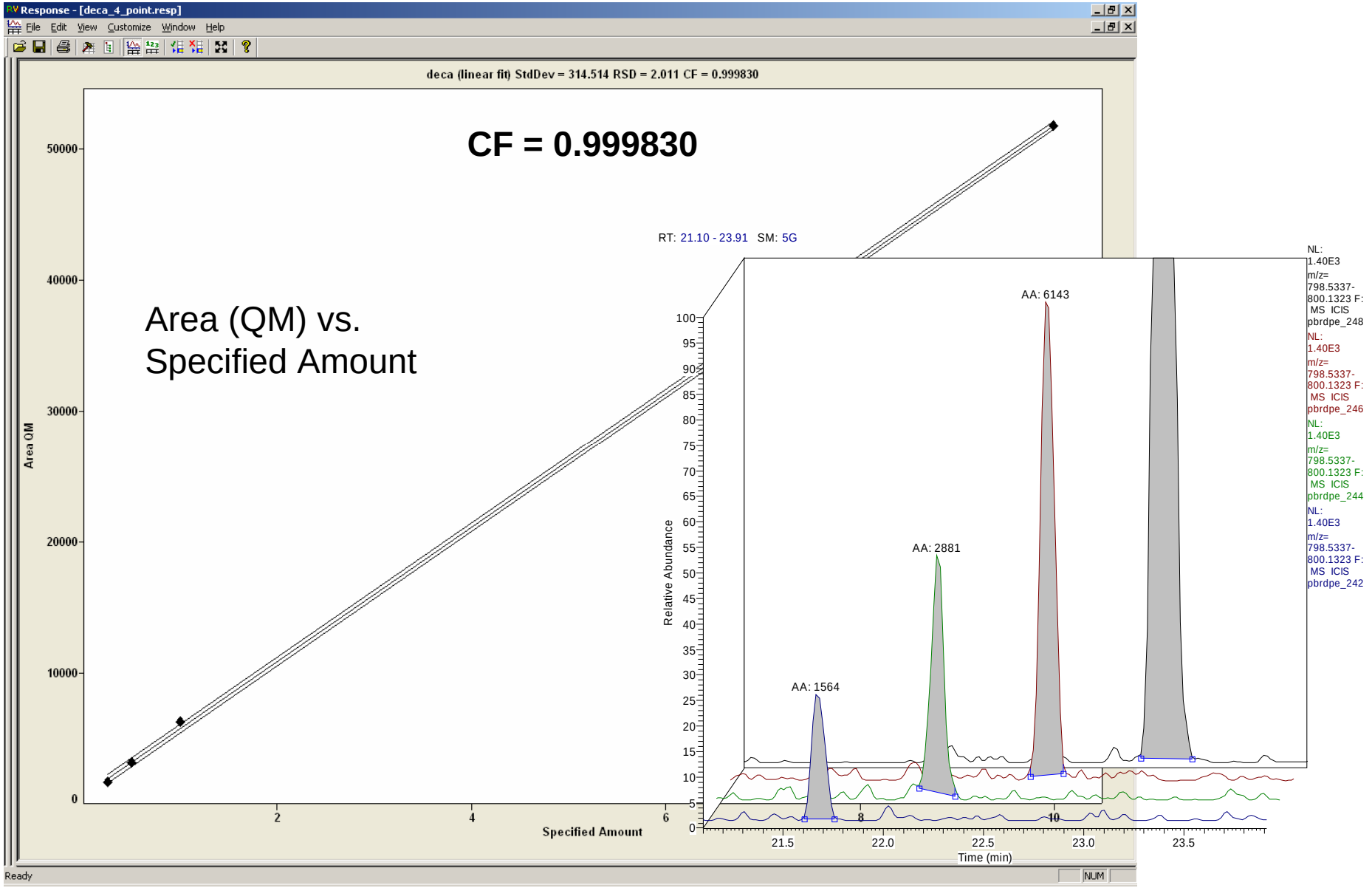


DB5 15 m; 0.25mm; 0.1 um
DB5 6 m; 0.2mm; 0.1 um

120 °C (2 min) –
15 °C/min -> 205 °C
-6 °C/min
-> 330 °C (15 m)
-> 305 °C (6 m)

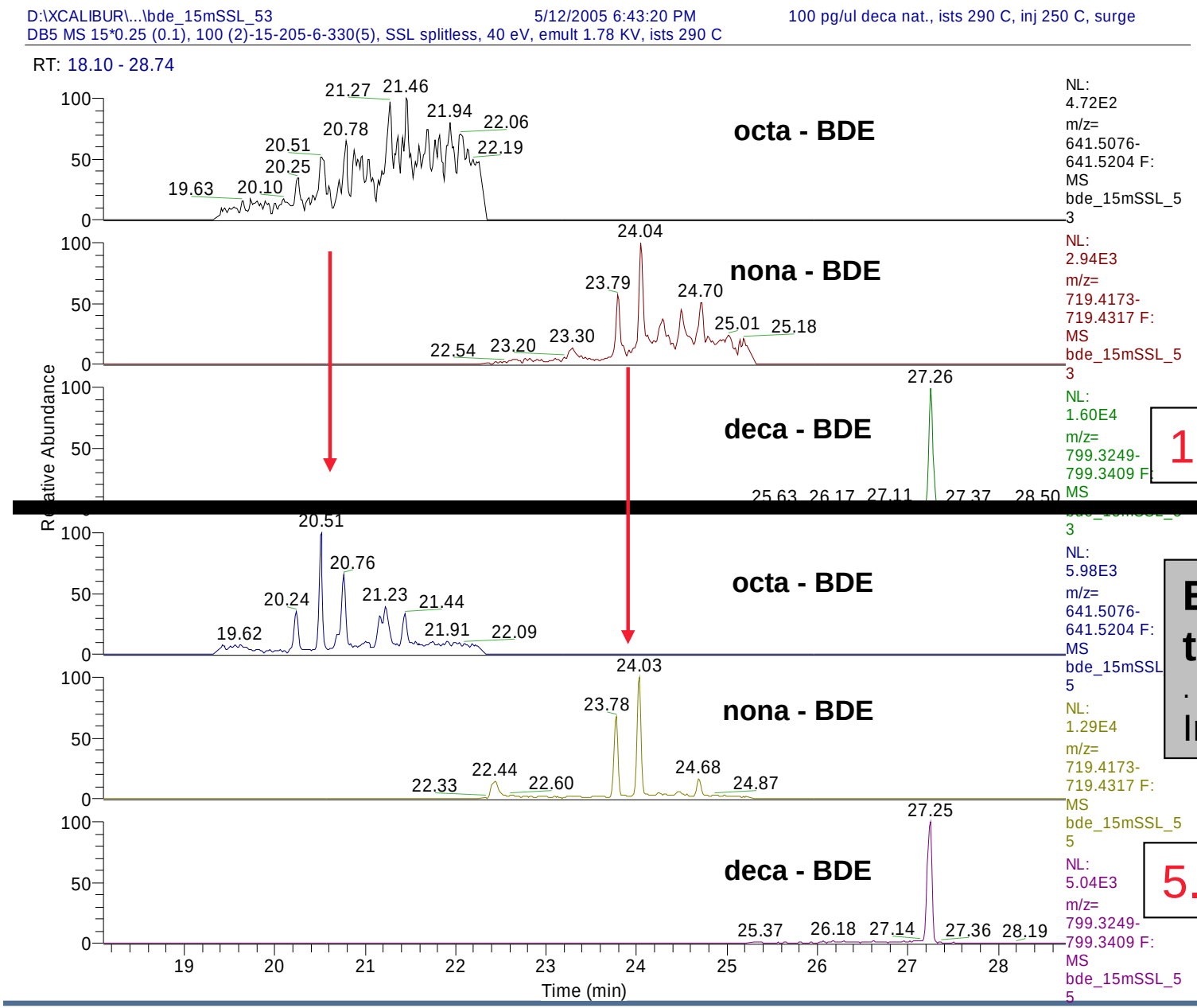
For display:
4 min offset on Ret. Times
of 6 m Chromatogram

Deca–BDE linearity on 6m column
(dual column setup) / 0.25, 0.5, 1, 10 pg native Deca)



Thermal degradation products of Deca-BDE

100 pg **native only BDE-209** was injected



Optimized splitless injection

for minimized thermal decomposition.

Injector temp.: 250 °C
Pressure pulse: 150 kPa

1.6 E4 deca peak height

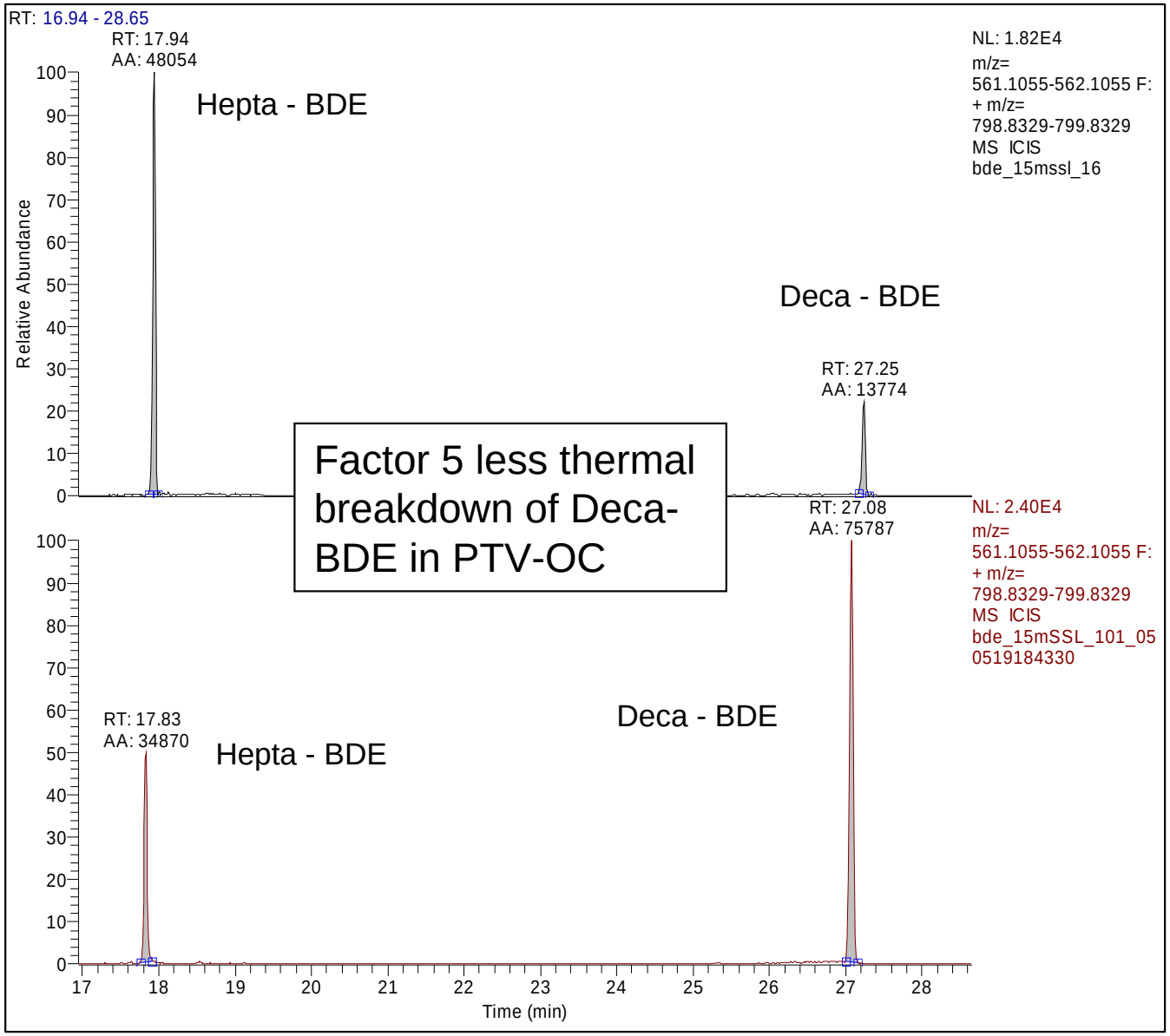
Enforced / increased thermal decomposition

.

Injector temp.: 310 °C

5.04 E3 deca peak height

Reducing thermal degradation of Deca-BDE in the injector
comparison Deca-BDE in splitless / PTV on column injection



DB5 15 m; 0.25mm;
0.1 um film
Flow: 1 ml/min He
Same oven program:
120 °C (2 min) –
15 °C/min -> 205 °C
- 6 °C/min -> 330 °C

Splitless injection
290 °C

no precolumn

PTV on column like injection

80°C(0.2)-5°C/min-
320 °C (20)

precolumn (1.8*0.53)

Conclusions

- estimation for Deca-BDE sensitivity with SSL/PTV:

30m:	**> 10 pg**
15m:	**ca. 1 – 5 pg**
6m:	**ca. 0.1 – 0.5 pg**

- dual column setup: combining **a.) good separation efficiency**
b.) sensitivity for Deca-BDE

- Deca thermal decomposition due to oven temperature probably reduced to the limit on 6 m column

- on column injection reduces decomposition in the injector strongly

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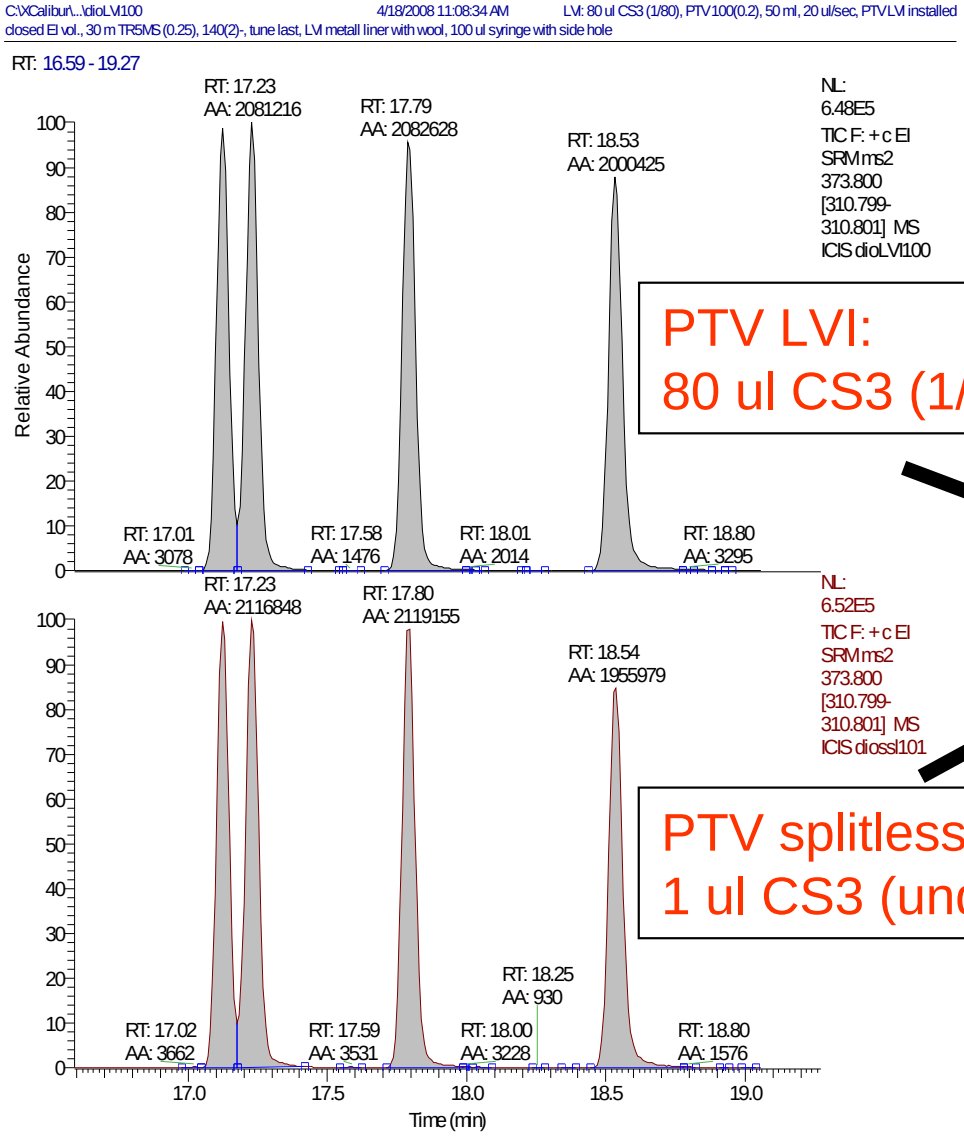
PTV LVI for POPs analysis

80 ul dioxins/furans with PTV LVI

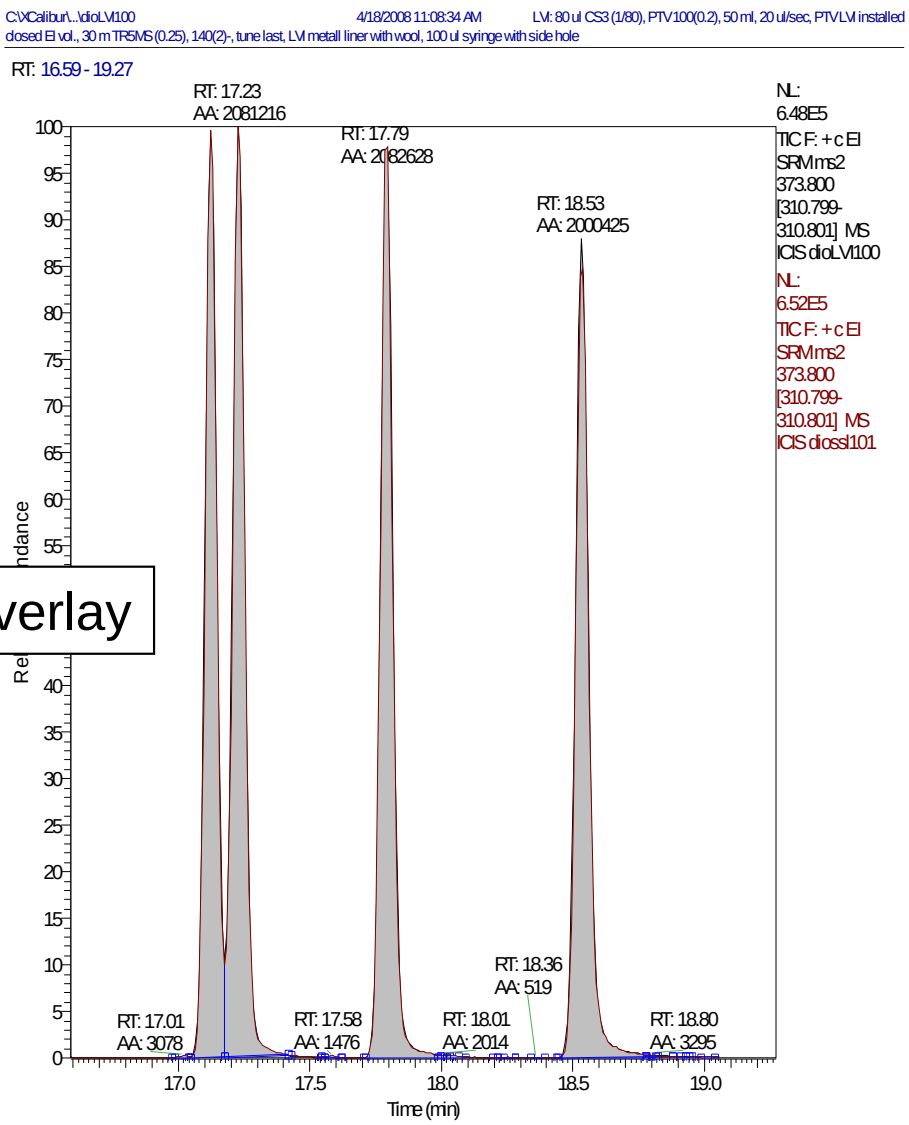
Recovery and peakshape



PTV LVI:
80 ul CS3 (1/80)

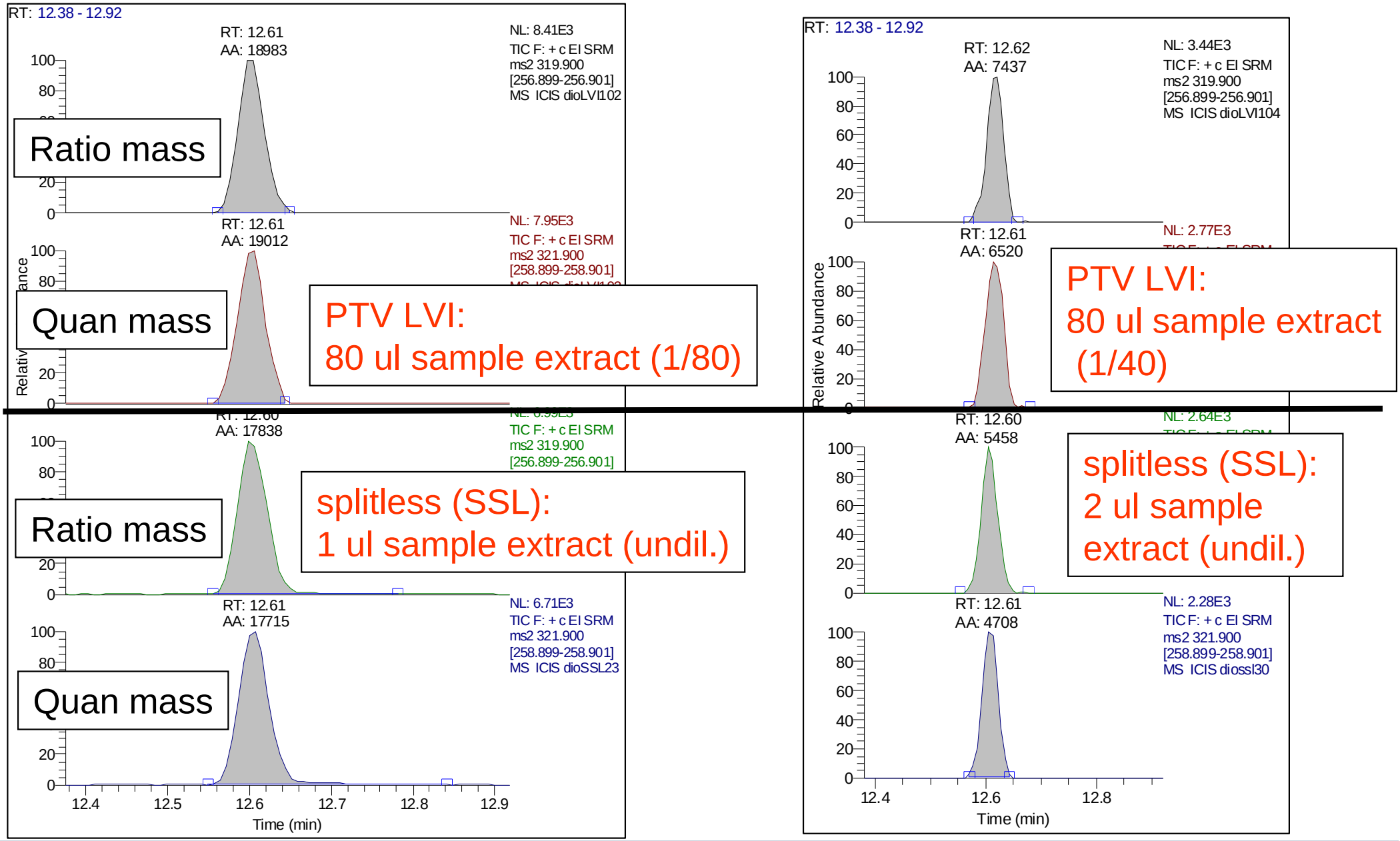
PTV splitless:
1 ul CS3 (undil.)

overlay



80 ul dioxins/furans PTV LVI on samples

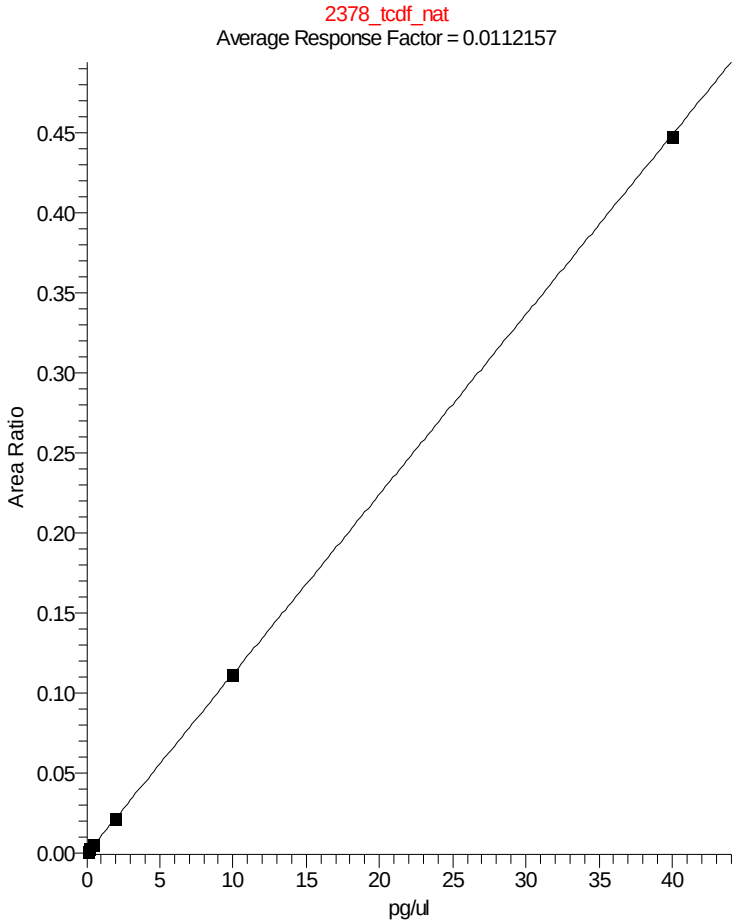
peregrine falcon egg extract / eal extract - tcdd



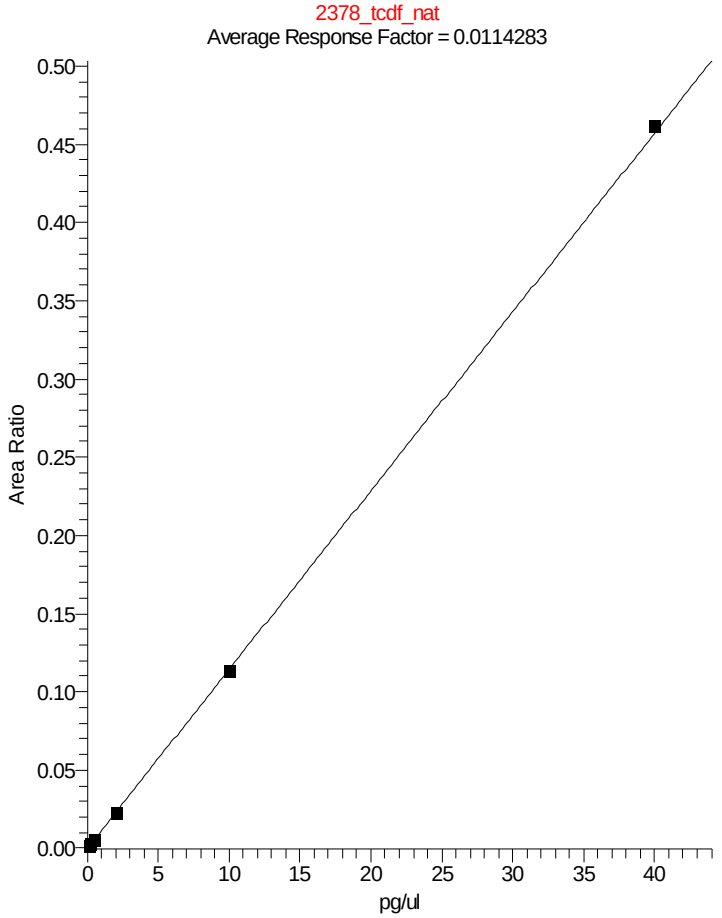
80 ul and 1 ul calibration curve: tcdf

average response EPA 1613 standards: CSL, CS 0.5, CS1 – CS4

80 ul calibration curve



1 ul calibration curve



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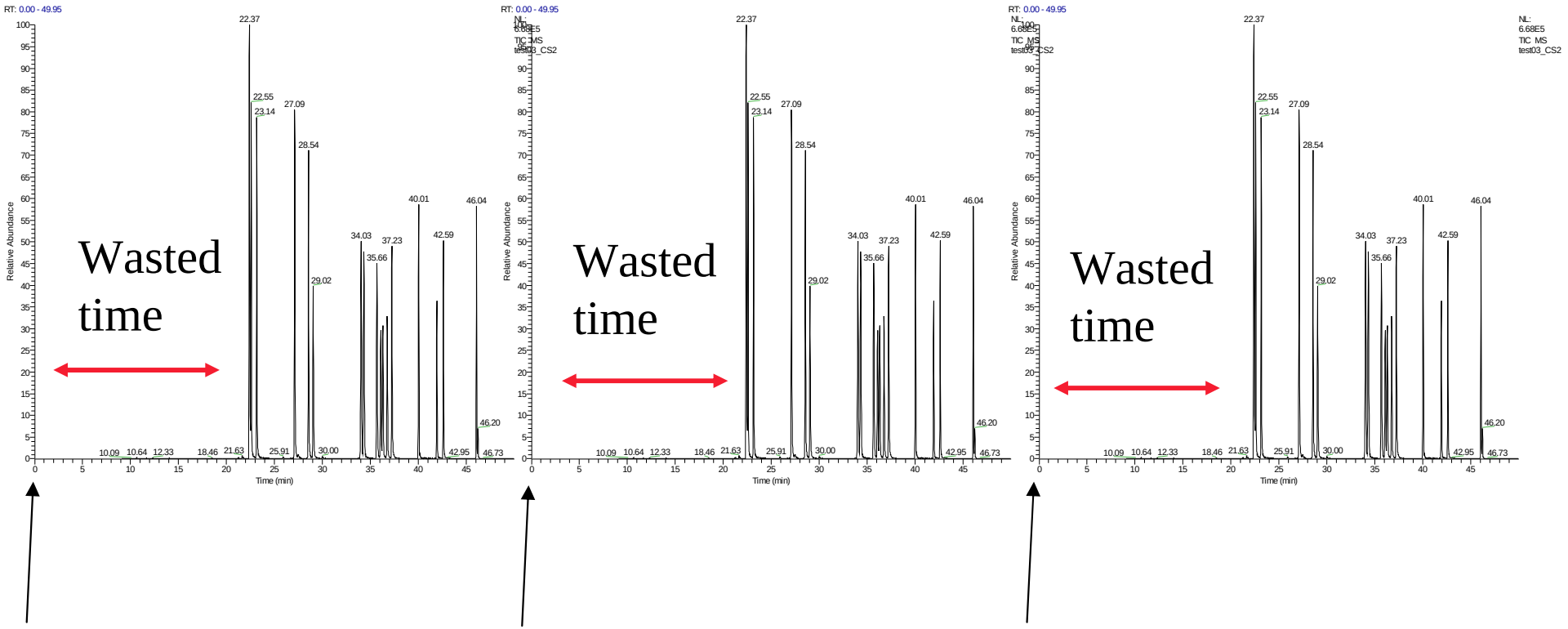
DFS dual data aquisition

DFS – Dual data option
up to two fold increased sample throughput

- **2 GCs attached to 1 DFS**
- **1 extra wide Autosampler covering both GC‘s**

The standard way to inject samples
single GC system: sequence of 3 injections

One GC



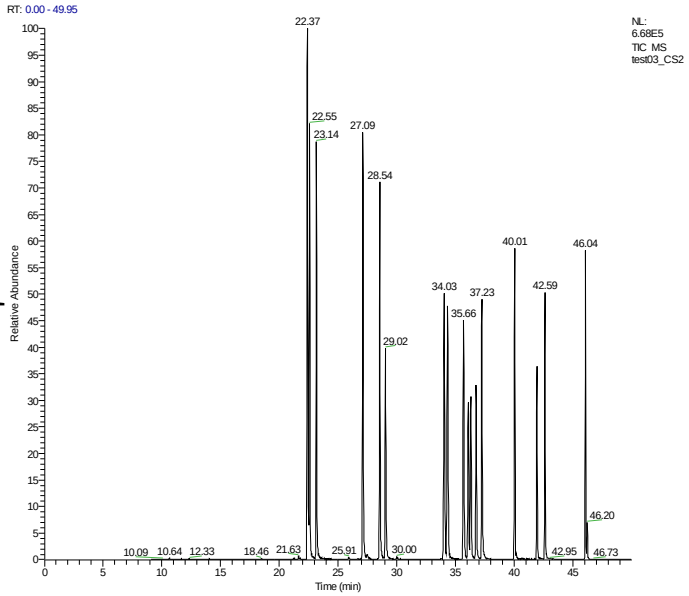
injection

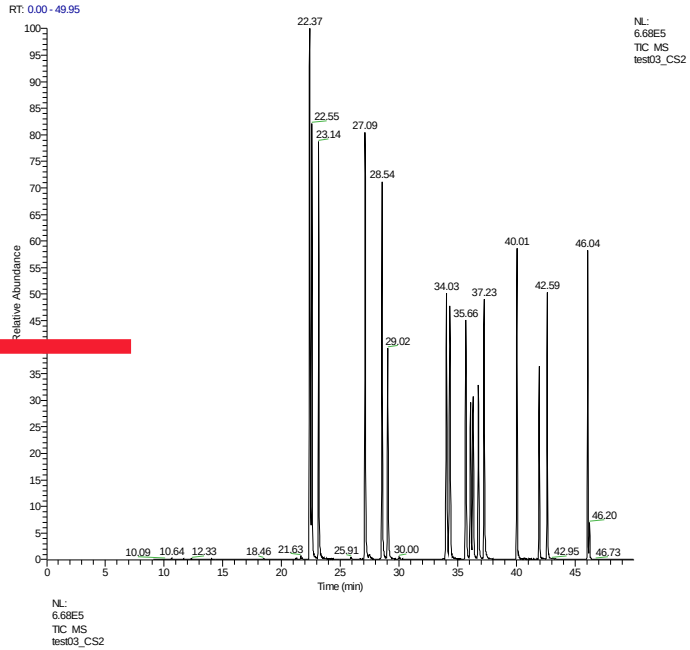
injection

injection

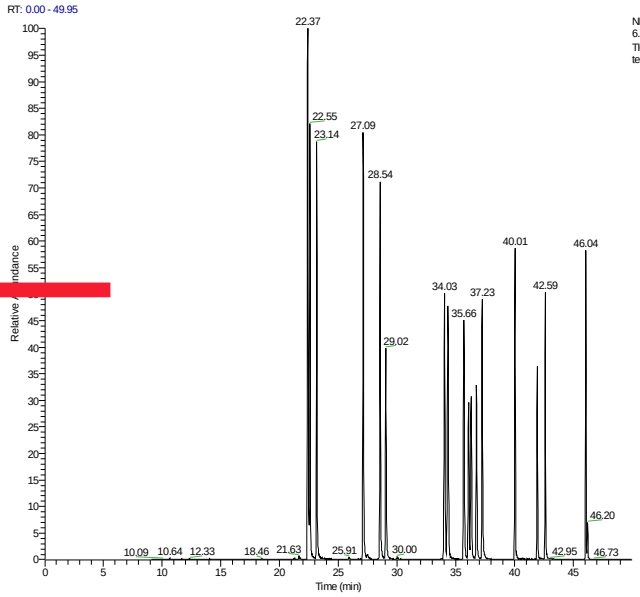
Dual GC system the standard way to inject samples
same time for 3 injections as on 1 GC system

GC1



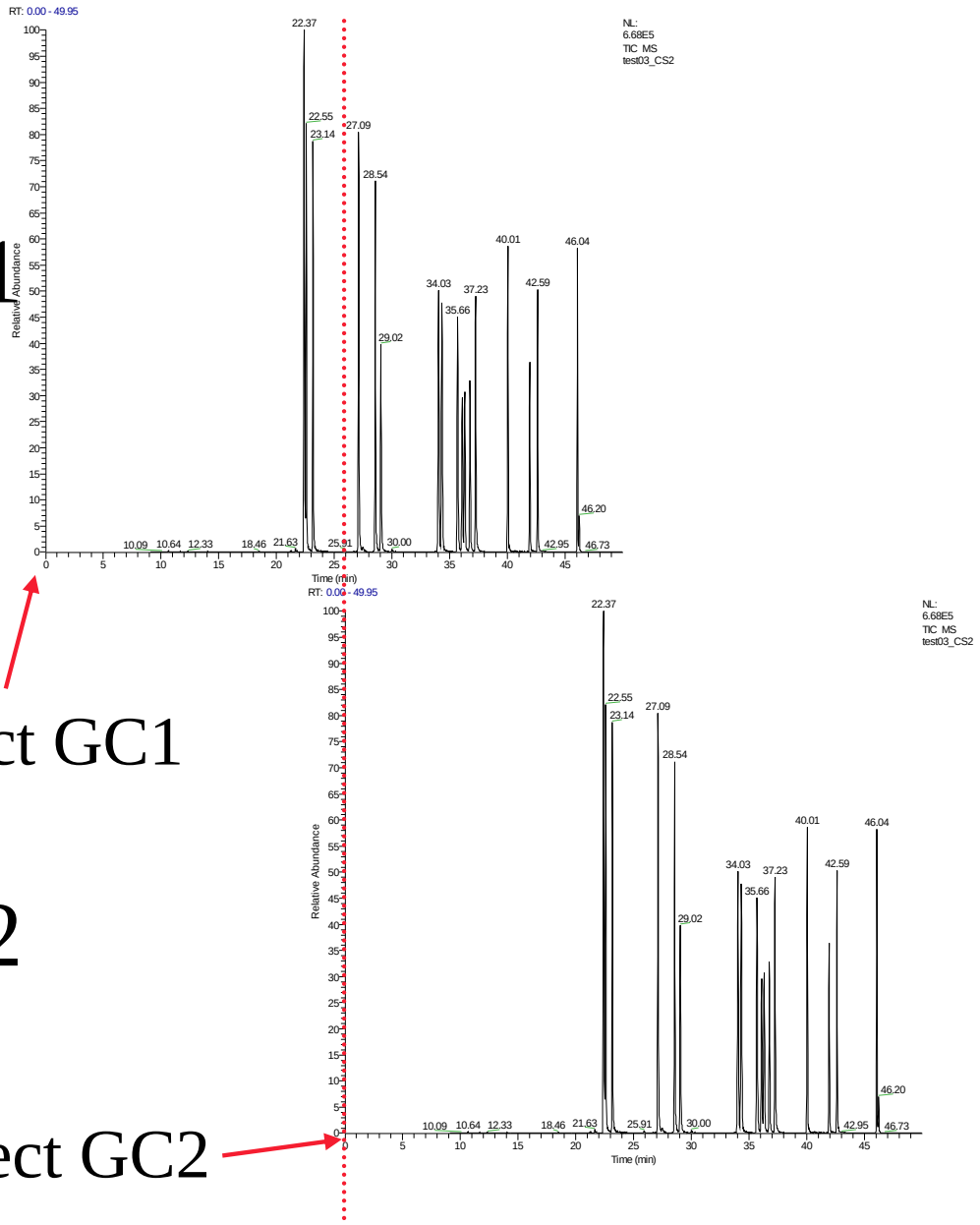


GC2



Dual Data aquistion – dual GC system
how to achieve higher throughput

GC1



Inject GC1

GC2

Inject GC2

➔ Staggered injection !!:

Inject next sample on GC2 already during elution of peaks on GC 1

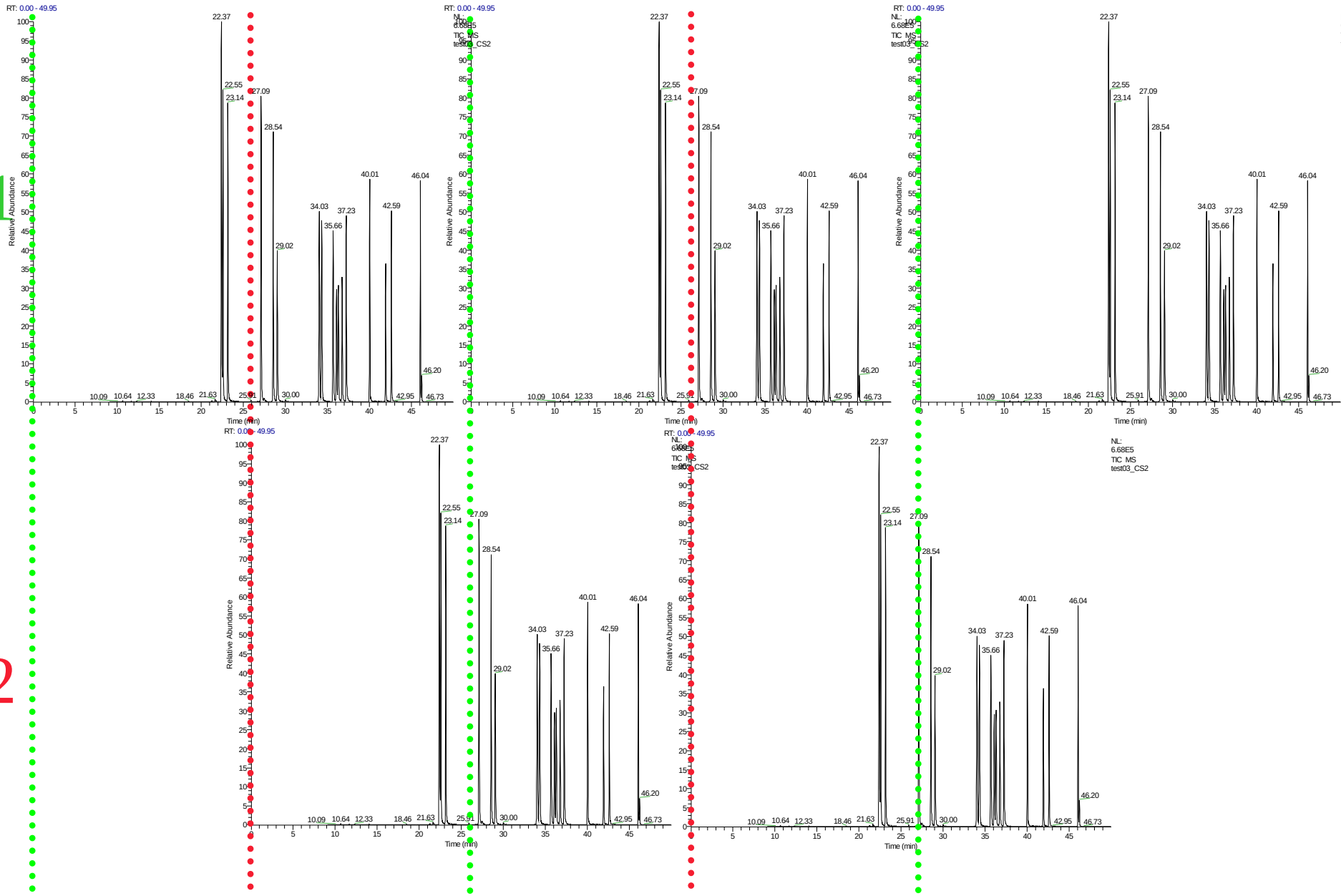
Red dotted line:
Injection time on GC2

Dual Data aquistion – dual GC system

5 samples injected in the same time as before 3

GC1

GC2

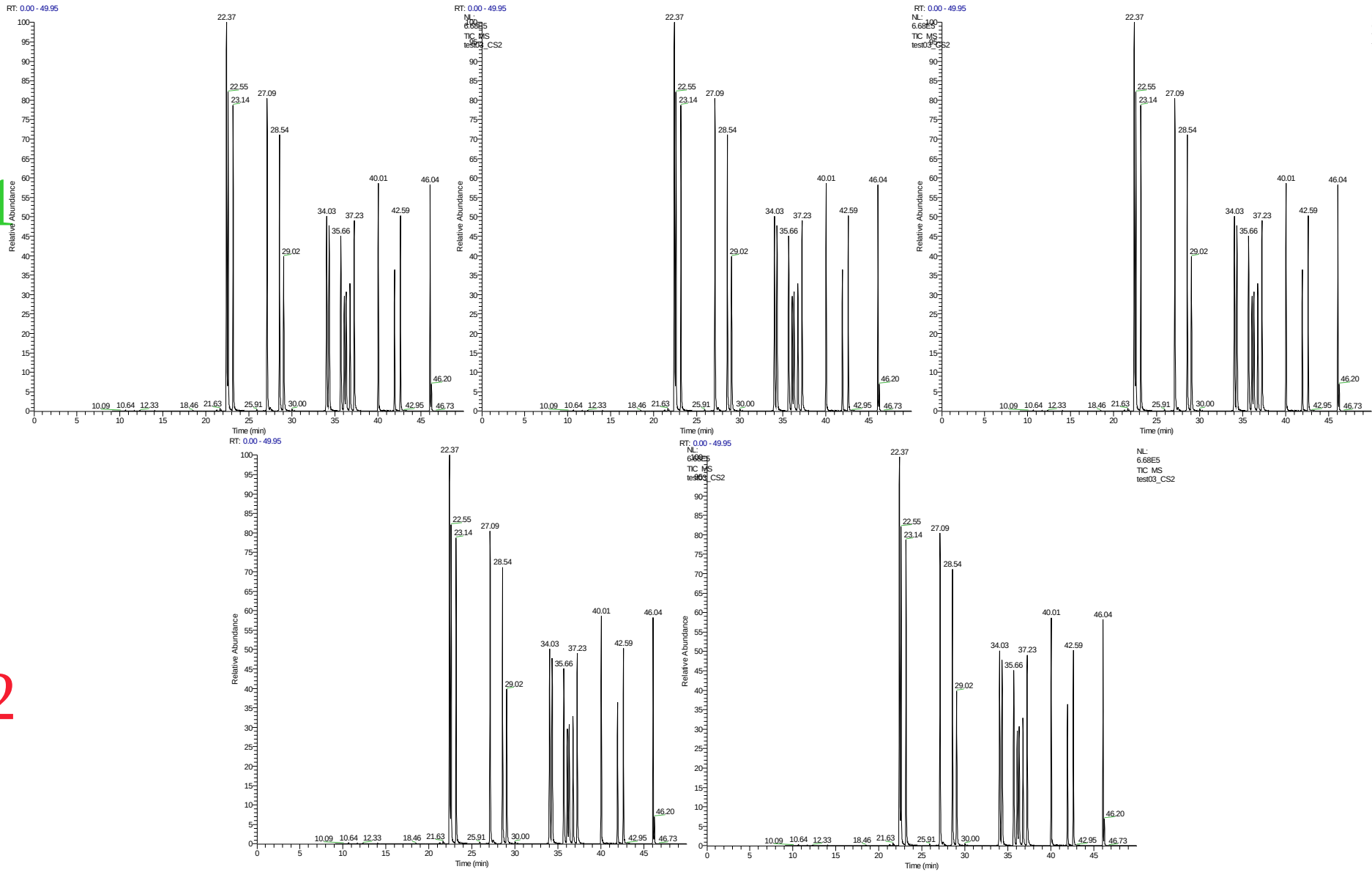


Dual Data aquistion – dual GC system

5 samples injected in the same time as before 3

GC1

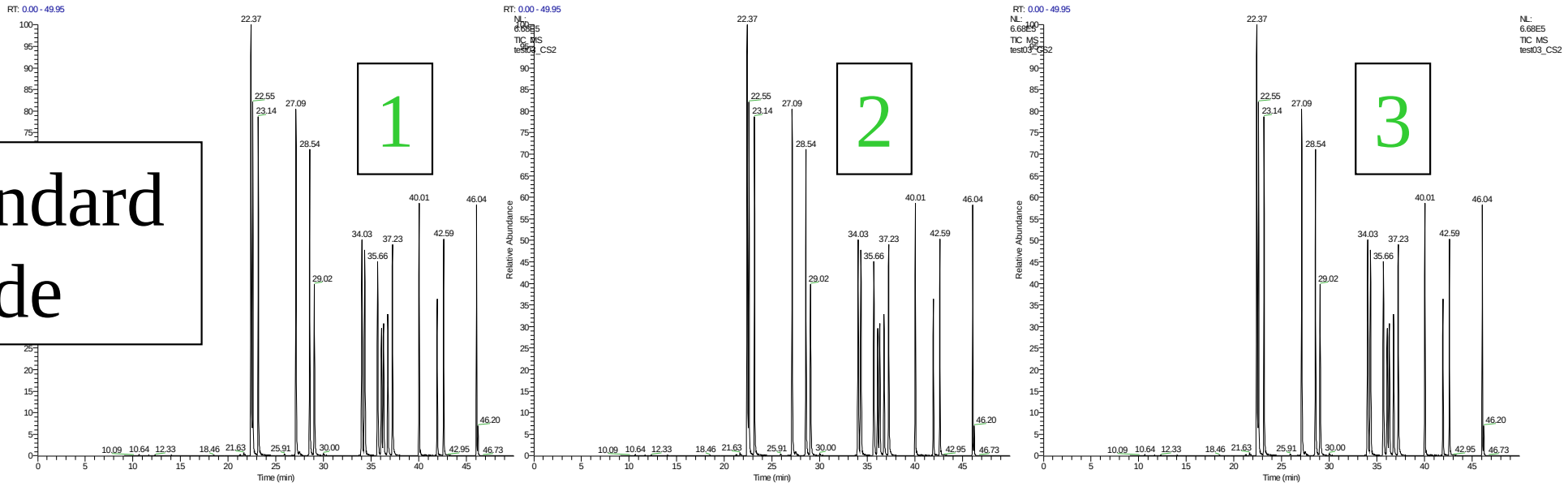
GC2



Dual Data aquistion – dual GC system

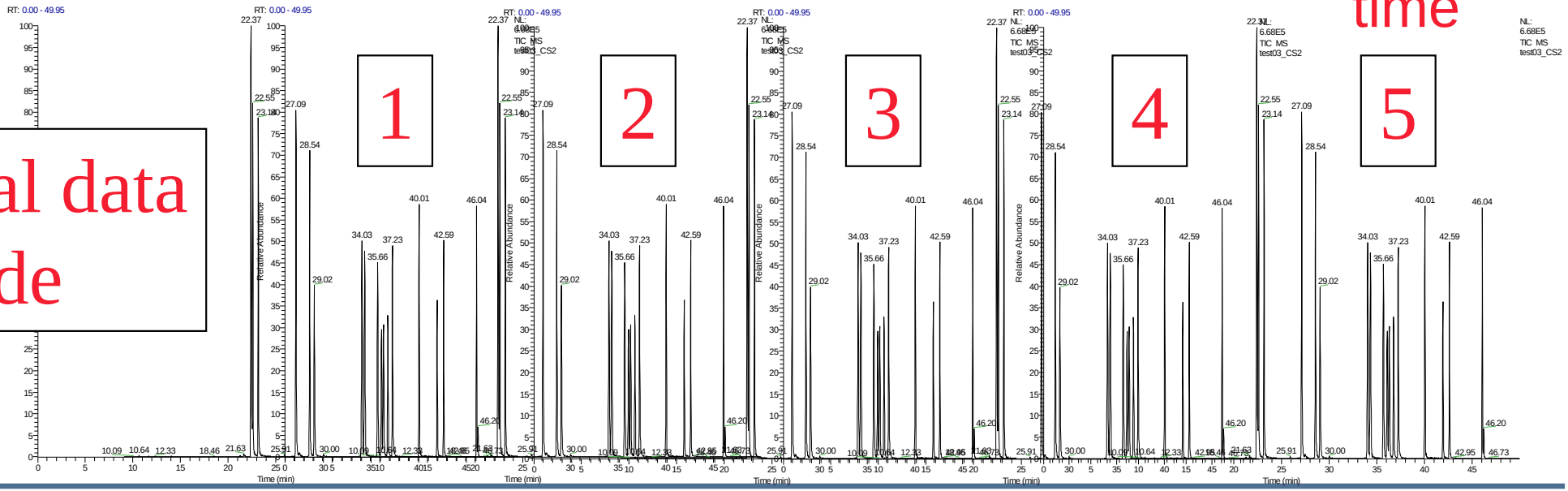
5 samples injected in the same time as before 3

Standard mode



time

Dual data mode



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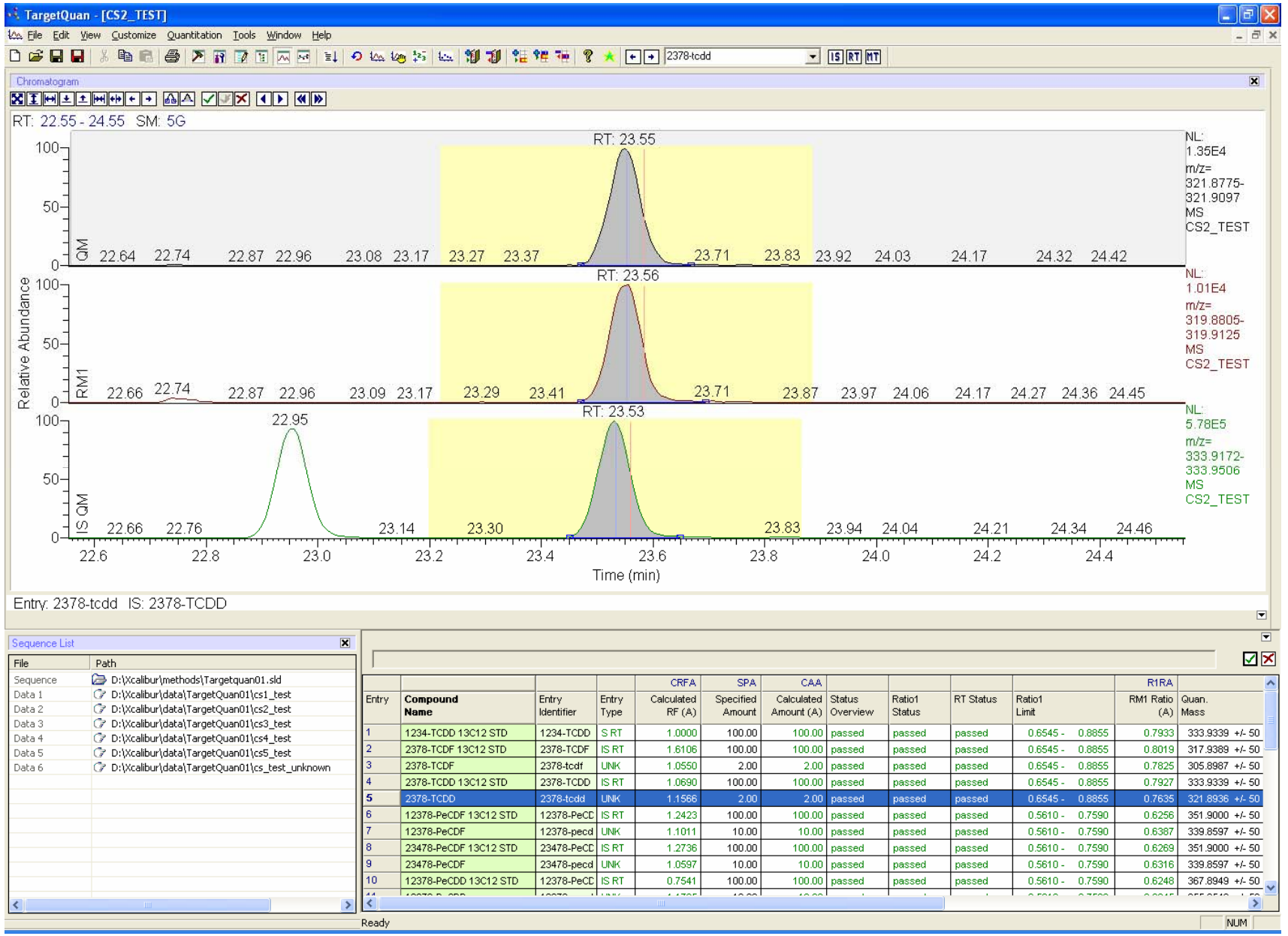
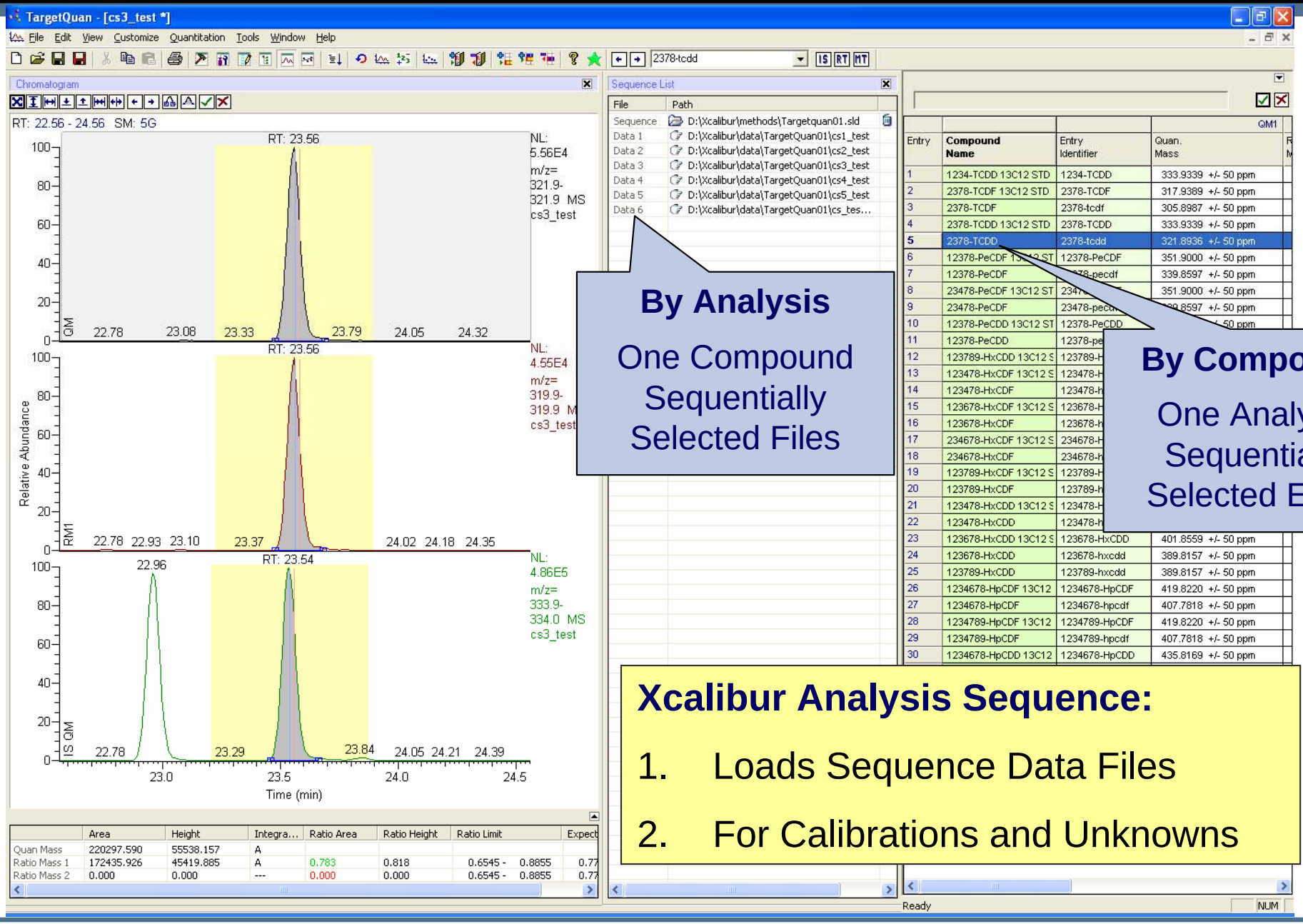
Targetquan: new Quantification software

TargetQuan – New Quantification Software package



TargetQuan – The New Peak Browser



By Analysis

One Compound Sequentially Selected Files

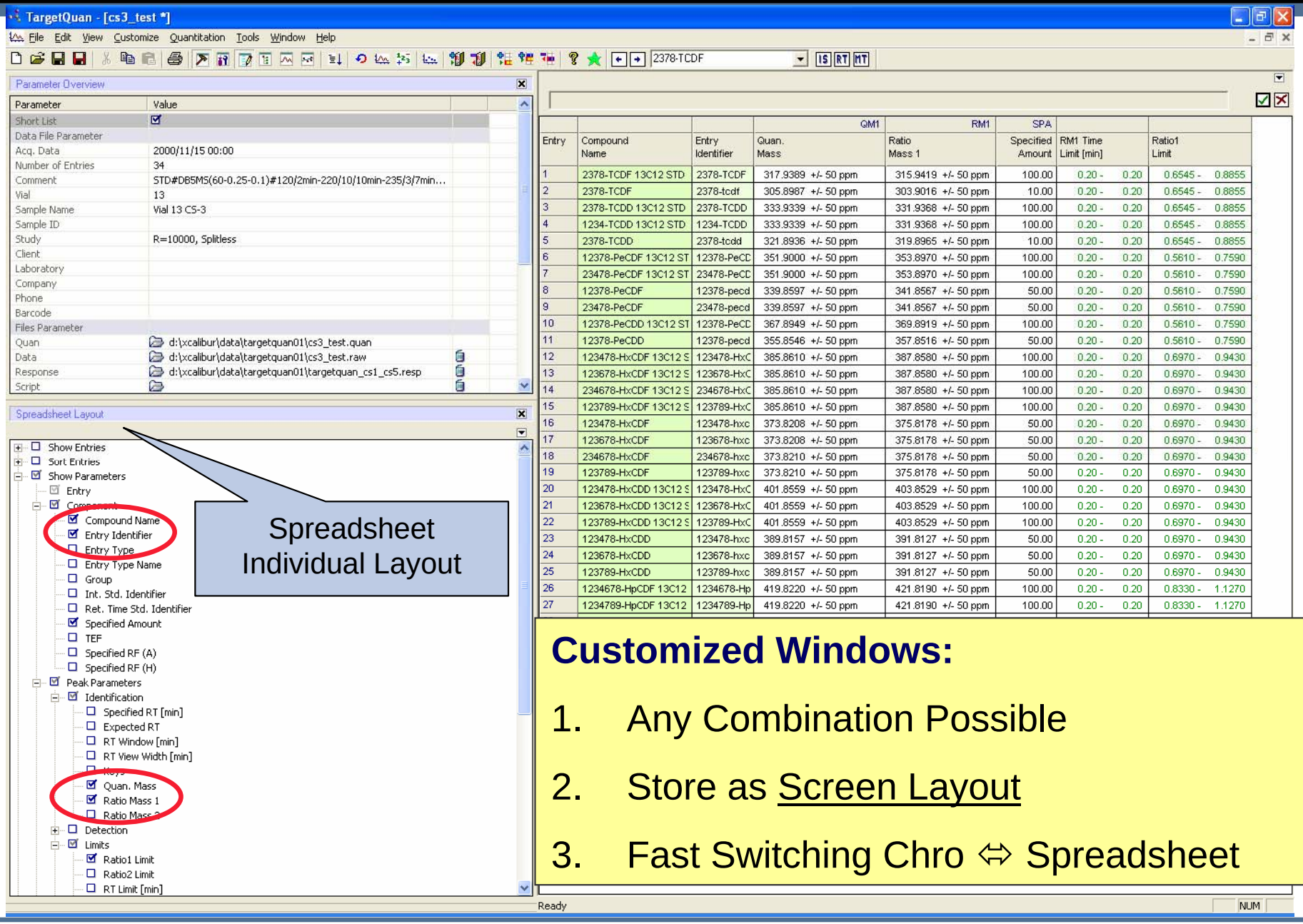
By Compound

One Analysis Sequentially Selected Entry

Xcalibur Analysis Sequence:

1. Loads Sequence Data Files
2. For Calibrations and Unknowns

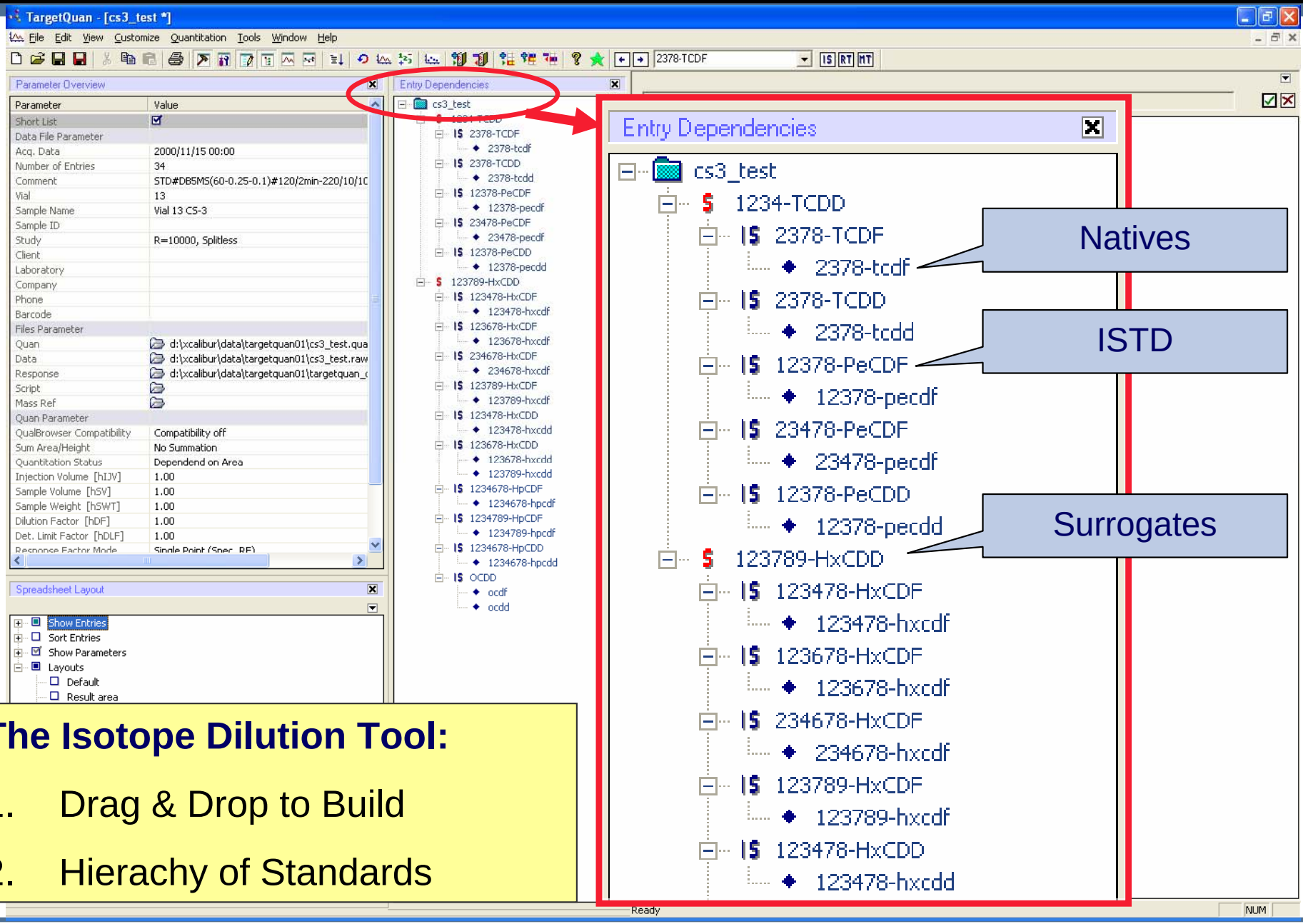
TargetQuan – The New Screen Layout



Customized Windows:

1. Any Combination Possible
2. Store as Screen Layout
3. Fast Switching Chro ⇔ Spreadsheet

TargetQuan – The ISTD Dependancy Tree



The Isotope Dilution Tool:

1. Drag & Drop to Build
2. Hierachy of Standards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