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New Possibilities for Targeted and Untargeted Contaminant Analysis in Environmental Samples

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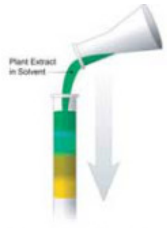
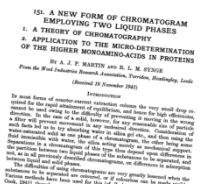
GC-MS Until Now




A NEW FORM OF CHROMATOGRAM EMPLOYING TWO LIQUID PHASES

Mikhail Tsvet 1903
Column chrom.

James, Martin
GC
1941-1951

First commercial
GC/Sector MS
Hitachi 1963

First commercial
GC/Quad MS
Finnigan 1967

First Commercial
GC/Triple Quad MS
Finnigan 1981

First Commercial
GC/TOF MS
Various 1995-2005

GC

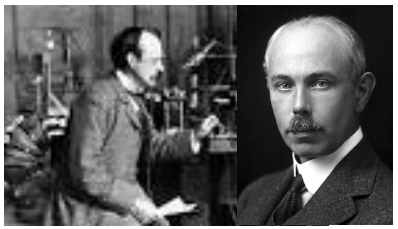
MS

1950s | 1960s | 1970s | 1980s | 1990s | 2000s | 2010s

Commercialisation of GC/MS

Majority Adoption of GC/MS

Thomson & Aston 1912-1919
Mass spectrometry



Gohlke & McLafferty 1957
GC/TOF MS
Holmes & Morrell 1957
GC/Mag. Sector MS

Ledford, Gross, et al. 1980
GC/FT-ICR MS

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GC-MS Until Now

Challenge

Limited GC-MS analysis

- No comprehensive quantitative & qualitative analysis
- For quantitation: targeted approaches required
- HR/AM Qualitative approaches compromised

Compromised Options

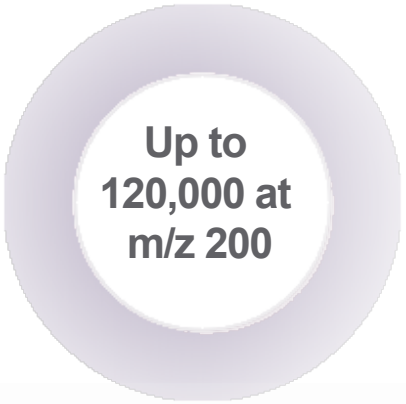
Multi-instrument approach

- Can be inefficient, convoluted and complicated
- GC single and triple quadrupole MS for target quantitation
- GC- Time-of-flight (Tof) MS with limited performance

Breakthrough in GC-MS capability

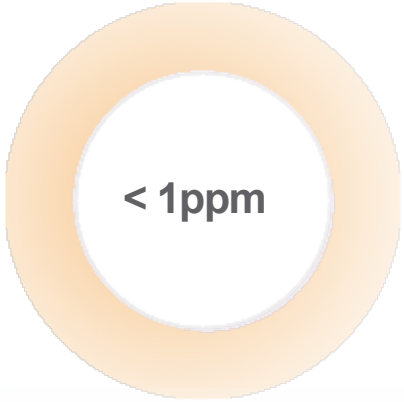
The Power of Q Exactive GC

Resolution



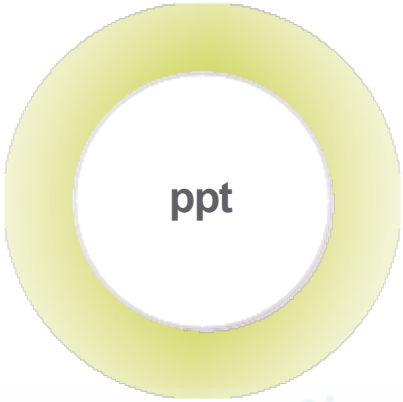
- Highest available
- Maximum selectivity
- Fast enough for GC!

Mass Accuracy



- Every scan
- All concentrations
- In complex matrix
- Across the mass range
- Everyday!

Sensitivity



- In full scan
- High selectivity
- High spectral fidelity

Dynamic Range

- Excellent coverage in sample profiling
- "Triple quad grade" quantitation in full scan

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Breakthrough in GC-MS capability

Challenge

Limited GC-MS analysis

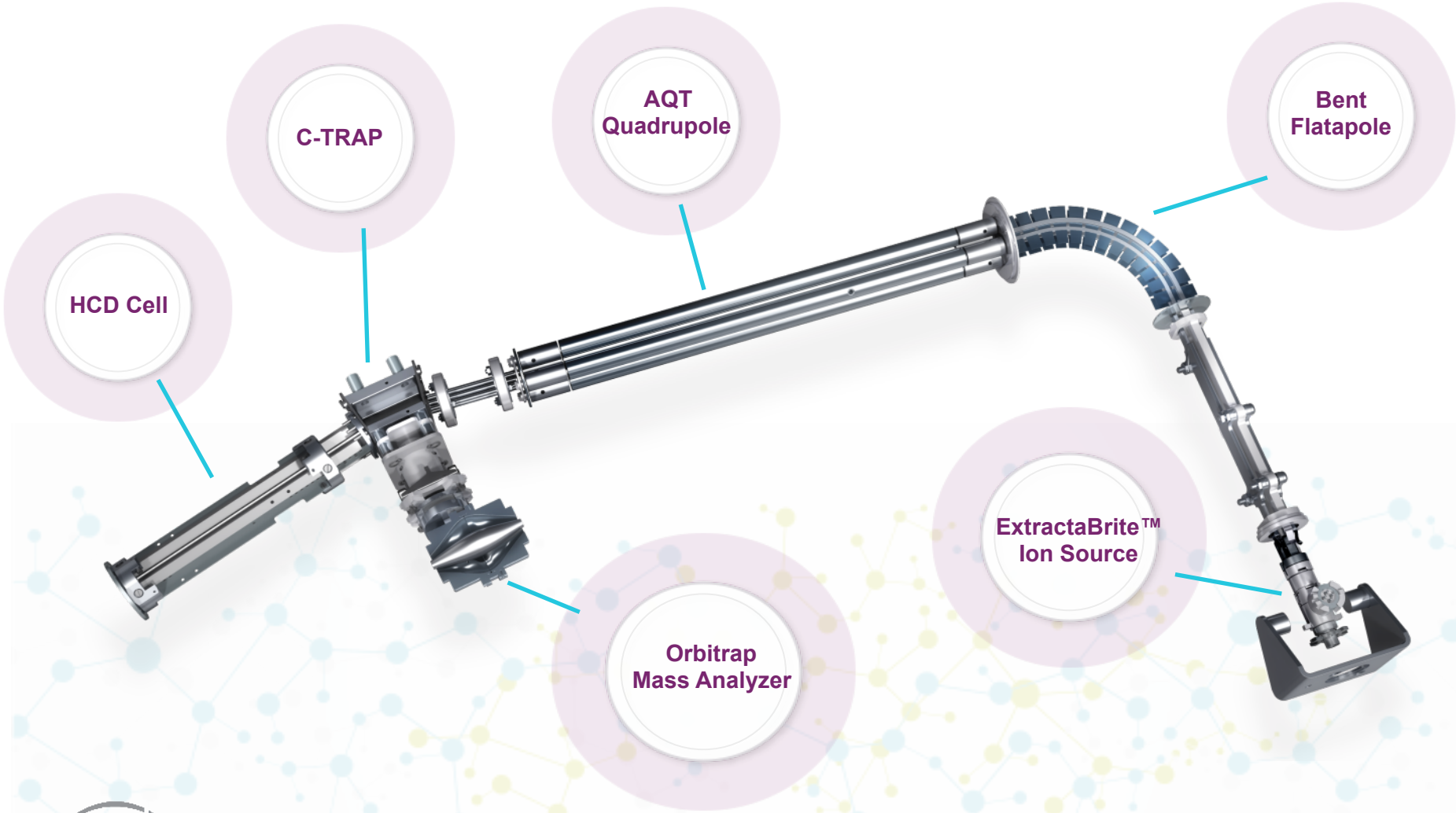
- No comprehensive quantitative & qualitative analysis
- HR/AM Qualitative approaches compromised
- For quantitation: targeted approaches required

Q Exactive GC

Powerful GC-MS analysis

- Easy, full quantitative & qualitative analysis
- Superior qualitative analysis and uncompromised HR/AM performance
- Quantitation as good as best performing GC Triples

Bringing GC and Orbitrap Technology Together



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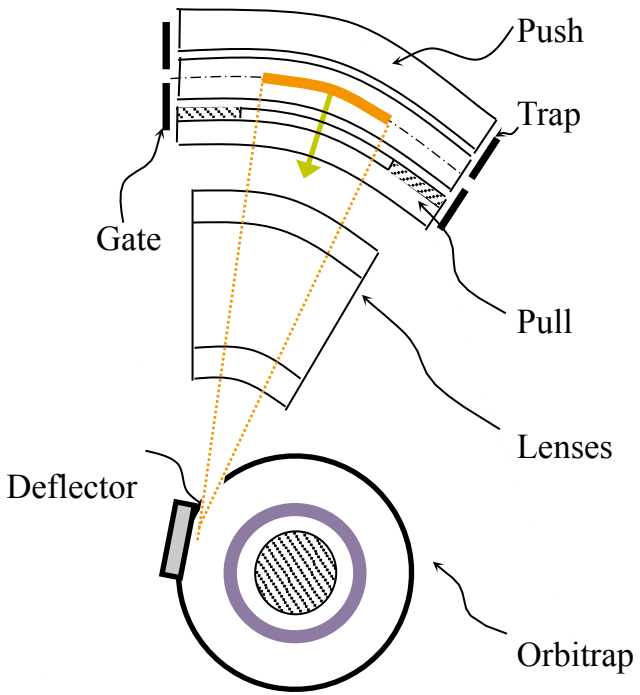
Pulsing Ions into the Orbitrap: Curved Linear Trap (C-trap)



- Ions are stored and cooled in the RF-only C-trap
- Ions are ejected along lines converging to the pole of curvature (which coincides with the Orbitrap entrance).
- As ions enter the Orbitrap, they are picked up and squeezed by its electric field

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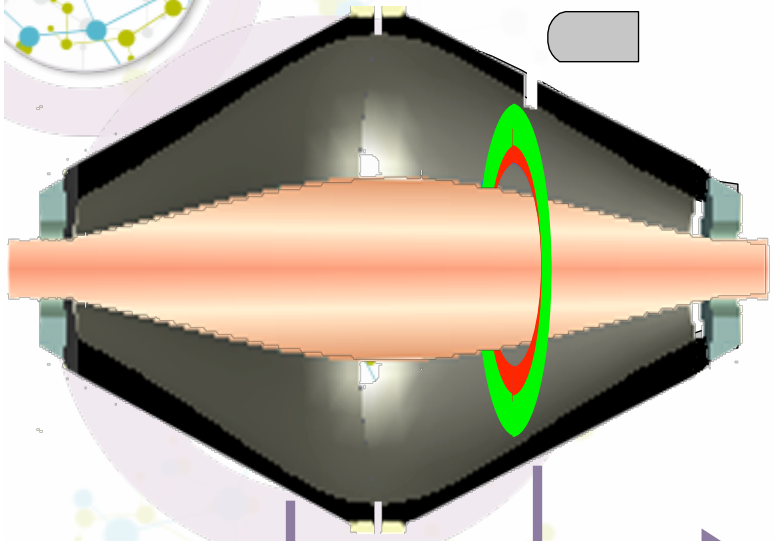
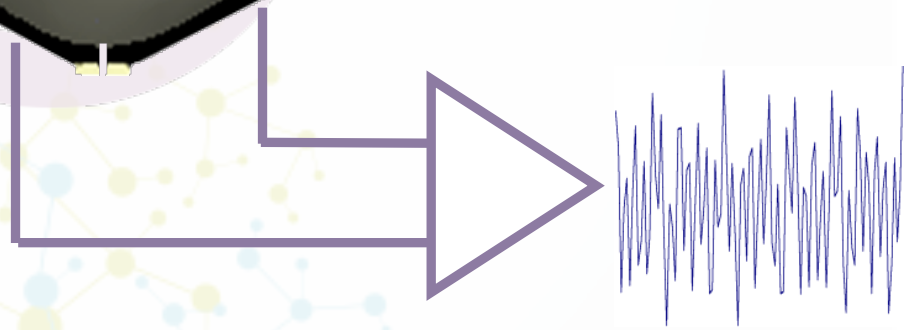
Retaining the Ions in the Orbitrap



$$\omega = \sqrt{\frac{k}{m/z}}$$



- Frequency of axial oscillations are independent of initial conditions of ions entering trap
- Therefore these oscillations used for mass determination
- Image current measured by outer split electrodes (no electron multiplier to replace!)
- Ion frequencies determine by complex superposition of measured ring oscillations through Fourier transform

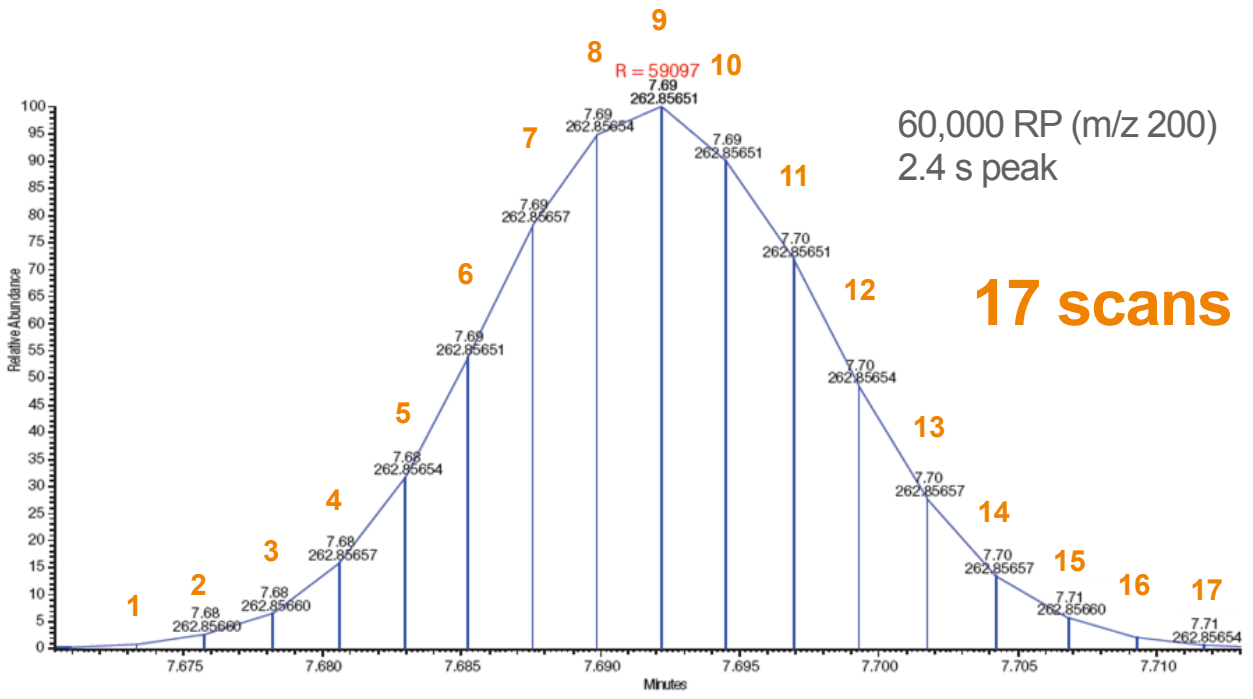
Breakthrough in GC-MS Performance

Highest selectivity and confidence with high resolving power

Fast acquisitions

- Important for accurate profiling of narrow GC peaks
- Full scan with resolving power of 60 (FWHM @ m/z 200) generates **17 scans**
- Fast enough for GC!

XIC of dieldrin in baby food (*m/z* 262.85642) 100ppb



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Breakthrough in GC-MS Performance

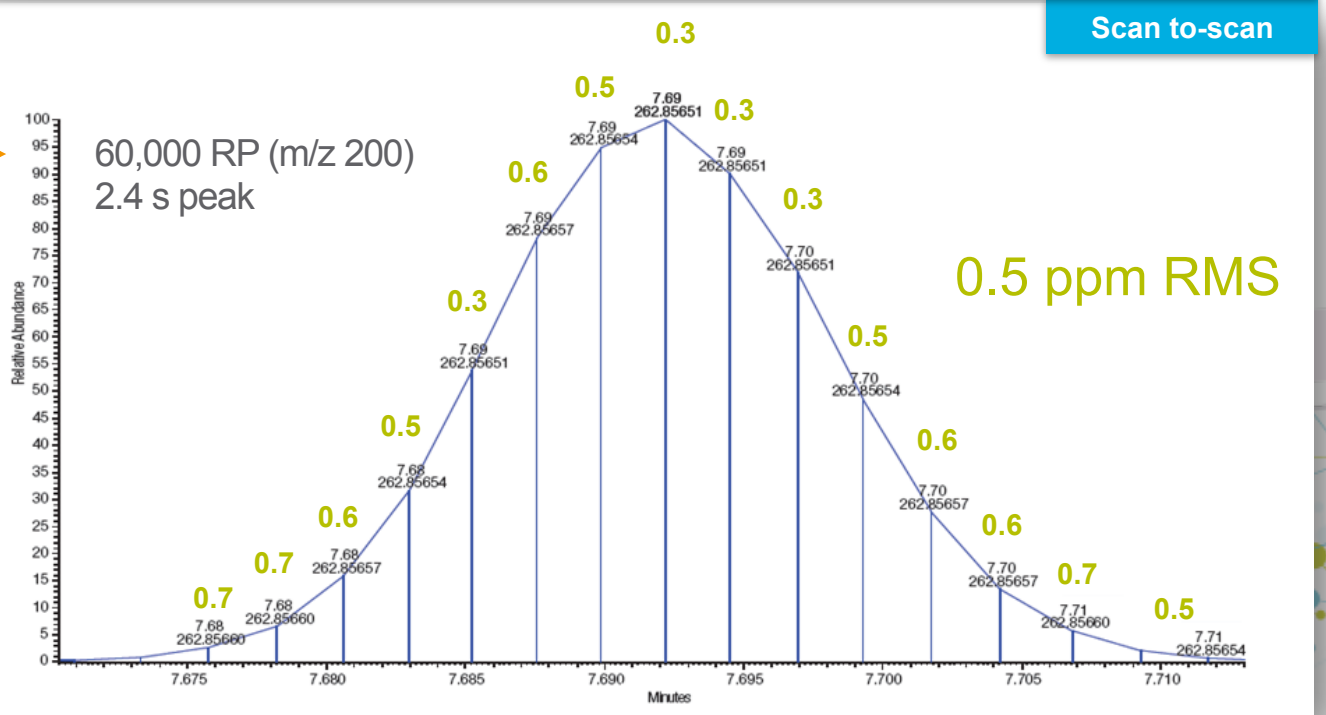
Consistently excellent mass accuracy

< 1ppm (internal)

< 3ppm (external)

- Scan-to-scan
- Low level in matrix
- Over full mass range
- Over full concentration range
- No need for continuously calibrating in sequence

XIC of dieldrin in baby food (*m/z* 262.85642) 100ppb



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Untargeted screening of environmental contaminants:

water iodinated disinfection by-products (DBPs)

Cristina Postigo Rebollo
Damia Barcelo

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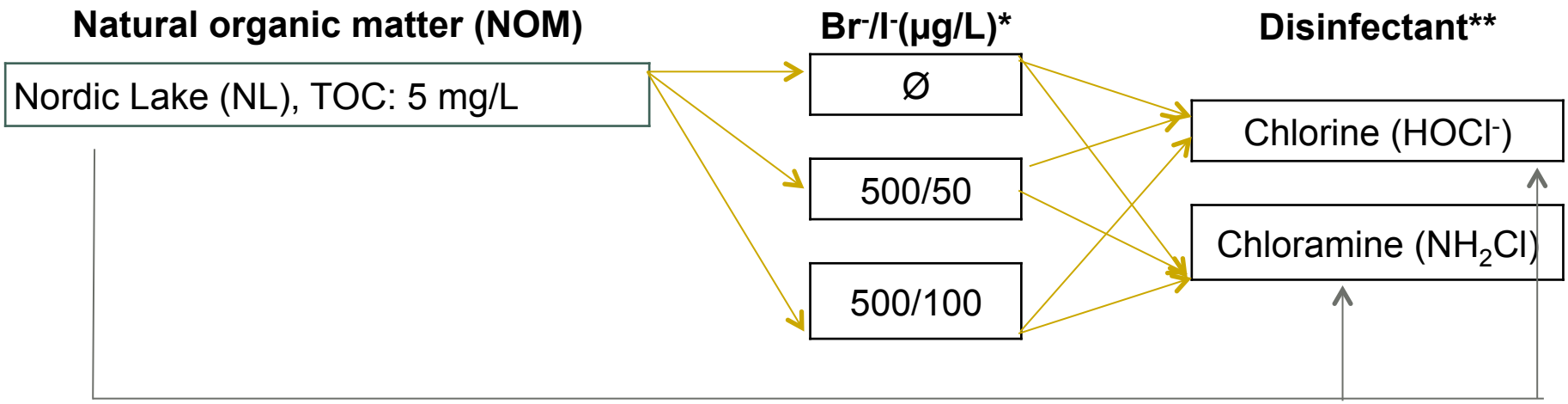
Screening of environmental contaminants: water DBPs

- Waters DBPs are formed when a chemical disinfectant react with the natural organic matter present in water.
- To date more than 600 DBPs have been already identified, and some of them pose a health risk as indicated by epidemiological studies.
- However, about 50% of the total halogenated material formed during disinfection treatments is still unknown.
- iodo-DBPs formed in chloramination processes are particularely cytotoxic and poorly characterized.
- These compounds are of concern for the environment and human health due to their potential toxicity.

GENERATION OF DBP MIXTURES (I)



*Bromine and iodine were added as KBr and KI, respectively.
**[Cl_2]=5 mg/L for SR, 4 mg/L for NL, 7.5 mg/L for LLOB, after chlorine demand test.

Reaction conditions:

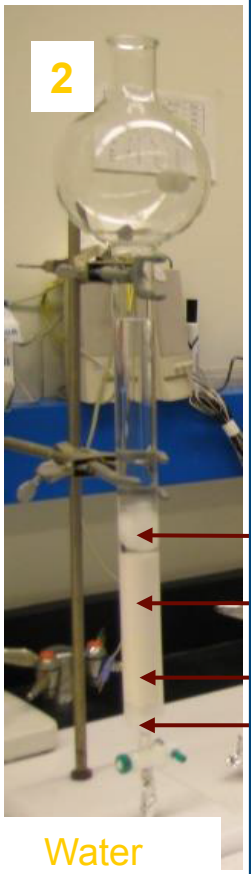
- **room T[a]**
- pH = **7.5** (phosphate buffer)
- stirring for **72 h**
- in the **dark**
- volumen = **17 L**

GENERATION OF DBP MIXTURES (II)

Sample extraction – XAD resin extraction

XAD resin purification

Chlorinated/ chloraminated water



Water extraction

Glass wool

XAD8 (24 mL)

XAD2 (24 mL)

Glass wool

1. Soxhlet extraction for purification of XAD resins (24 h with MeOH, 24 h with ethyl acetate, 24 h with MeOH).
2. Water extraction (16L) onto purified XAD resins.
3. Elution of analytes with ethyl acetate (224 mL).
4. Rotary evaporation of ethyl acetate extract (140 rpm, 35 ºC).
5. Evaporation under N_2 until 0.8 mL.
6. Diazomethane derivatization of half of the extract.

XAD resin extraction

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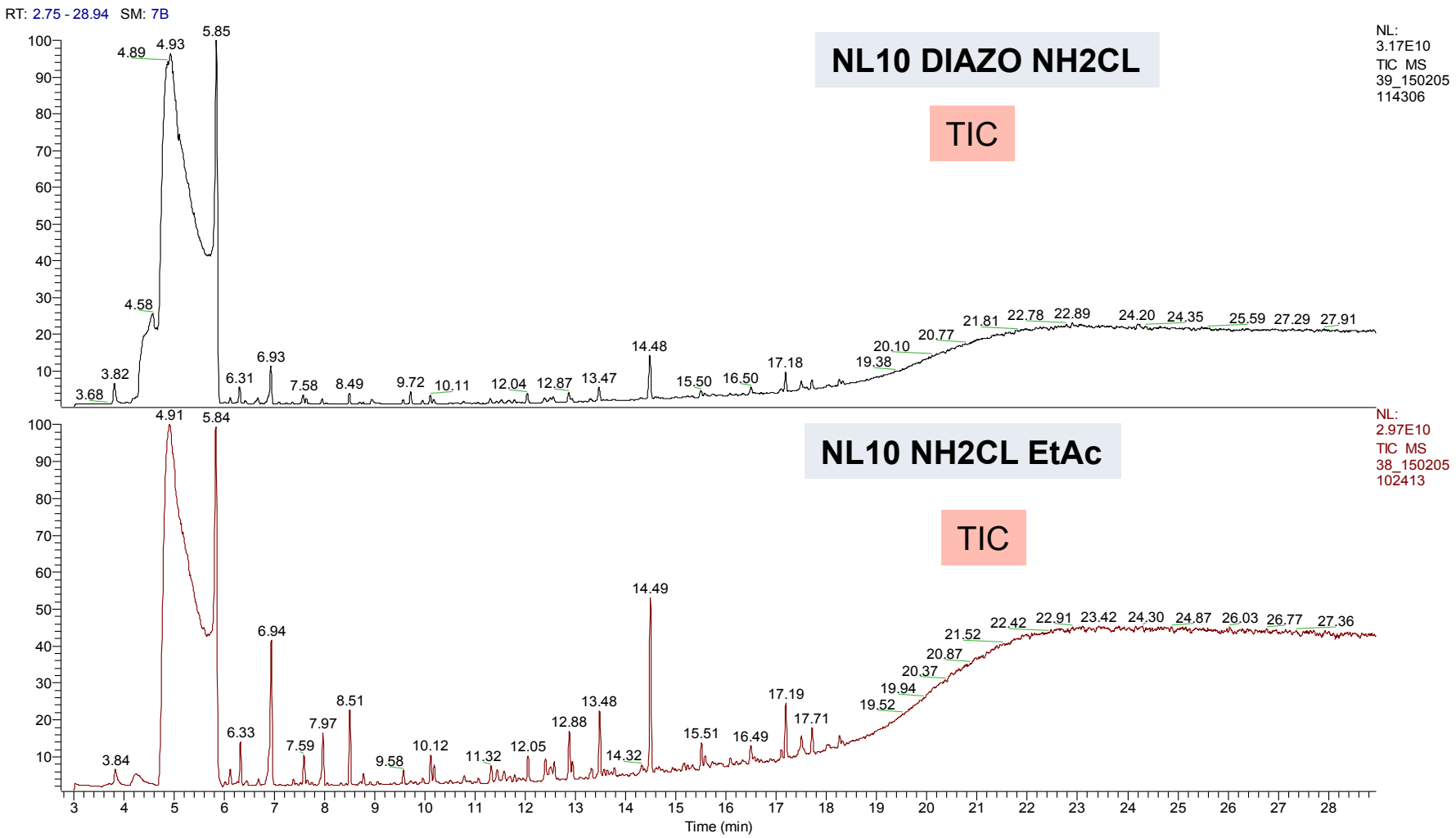
Samples were screened for iodine-DBPs



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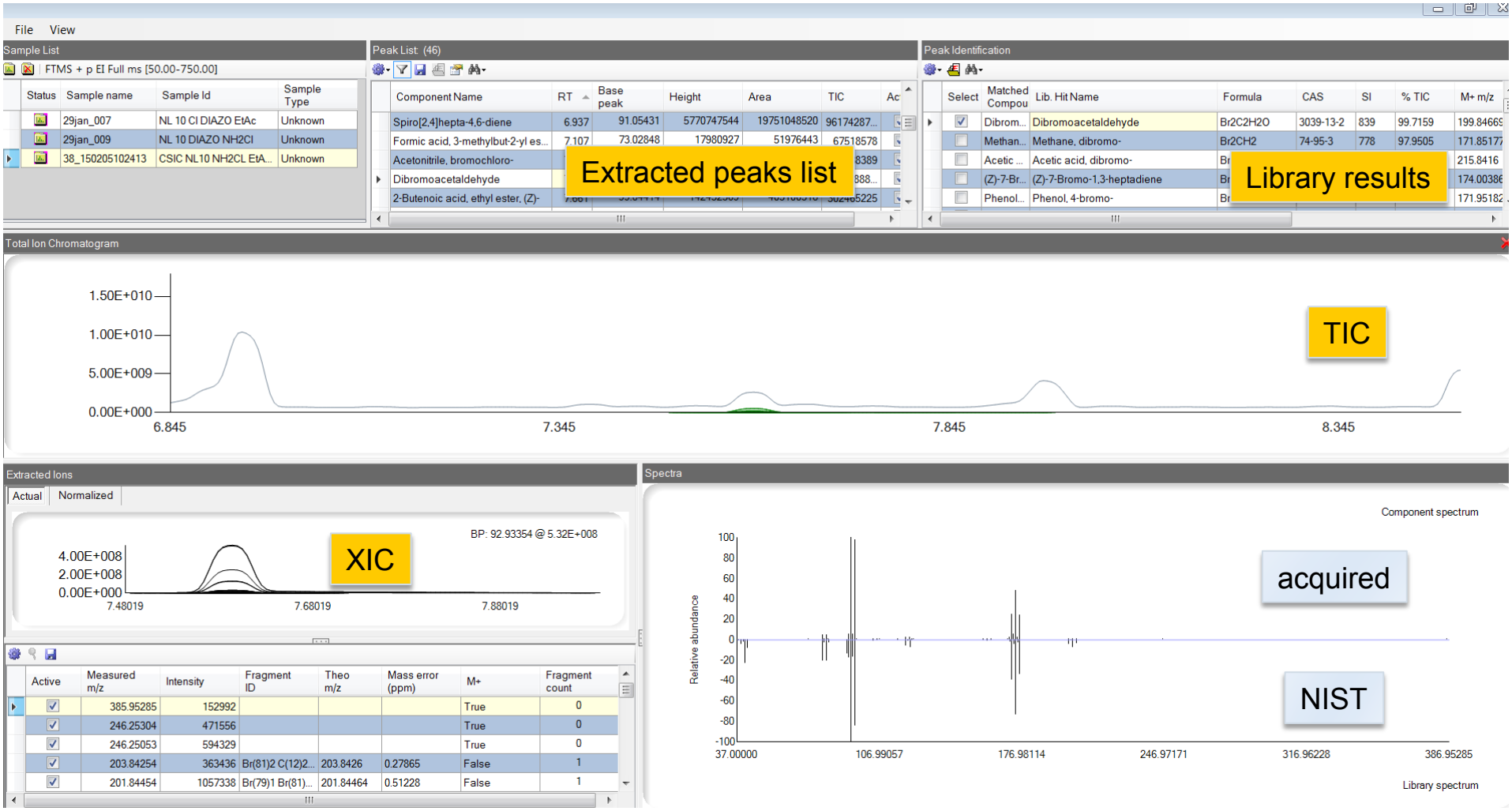
Deconvolution software Results Browser



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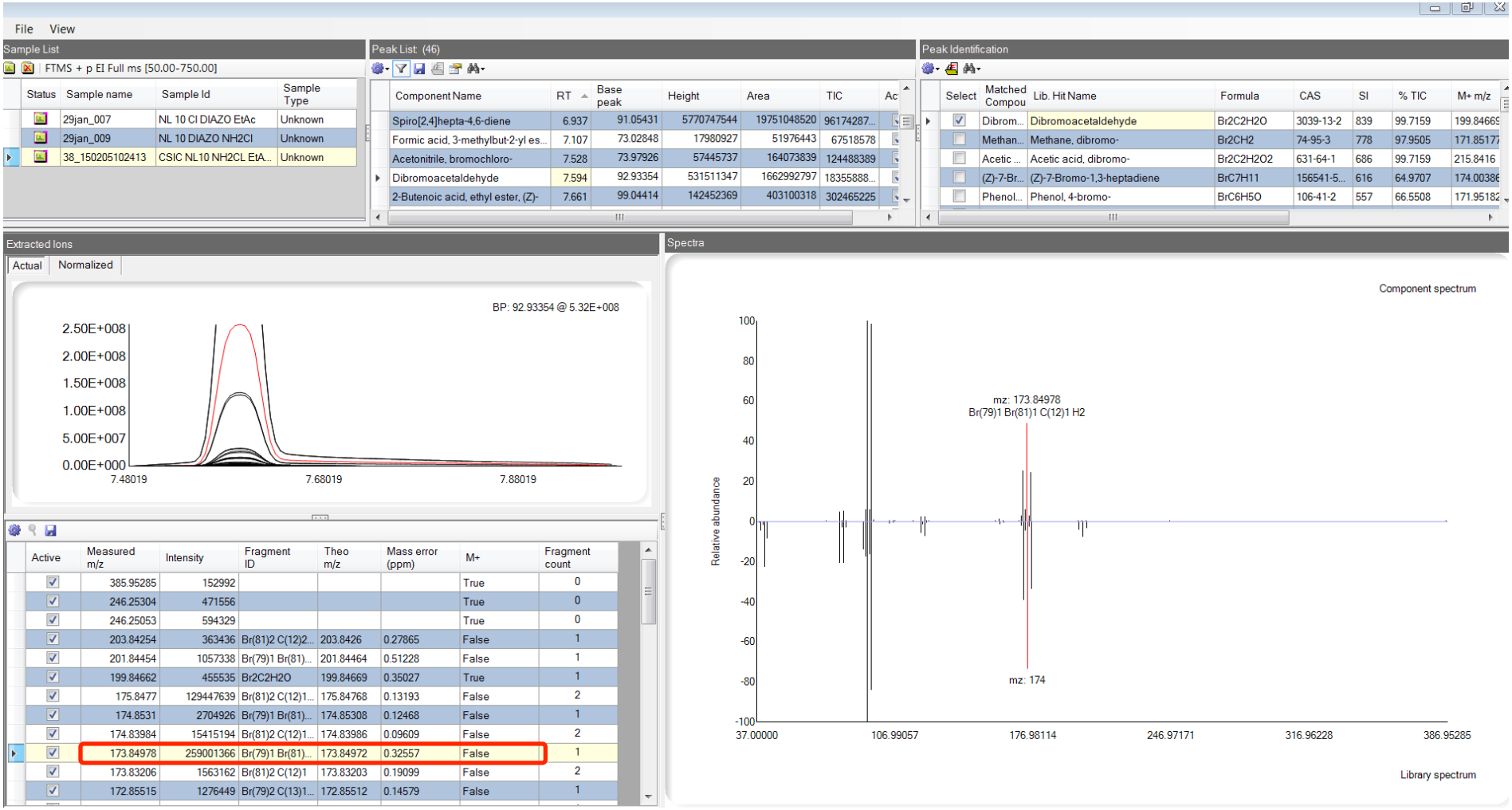
Dibromoacetaldehyde: intelligent candidate verification



Library search compatible with existing unit res libraries

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Example of compounds found in sample NL10 NH2CL EtAc (NIST ID)

25 unique compounds identified in the treated sample compared to blank

Component Name	RT	m/z	Area
Methane, bromo-	3.84	93.94136	2287289010
Ethyl bromide	4.19	109.95492	70878448
Dichloroacetaldehyde	4.21	83.95286	239462033
Methane, iodo-	4.26	141.92743	6835098508
Methane, bromo-	4.32	93.94136	79510322
Methane, bromodichloro-	6.45	82.94501	231940325
Acetonitrile, dichloro-	6.47	81.9372	27542835
Acetonitrile, bromochloro-	7.53	73.97926	164073839
Methane, dibromo-	7.59	92.93354	1662992797
Acetonitrile, dibromo-	8.78	119.92674	784206464
Ethyl iodoacetate	9.58	185.91718	1060392837
1-Bromo-3,3,3-trifluoroacetone	10.25	122.92638	17442292
3,4-Dibromo-1-pentene	11.31	67.05429	428945278
Benzene, 1-bromo-2,3-dimethyl-	11.44	105.06999	495067921
Threo-1,4-dibromo-3-pentanol	11.51	136.95973	103169909
Benzoic acid	11.58	105.0336	1259211272
Methane, bromodiiodo-	11.70	218.83012	288558451
Acetic acid, bromochloro-, methyl ester	12.45	128.89227	510614169
Benzene, 1-bromo-2,4,5-trimethyl-	12.87	119.08565	2366794432
Benzene, 2-bromo-4-methyl-1-(1-methylethyl)-	13.57	196.99606	331797666
Phenol, 2,4-dibromo-	13.78	251.86038	582559994
Phenol, 3-(2-bromoethyl)-	14.39	199.98312	32854422
Benzene, 2,4-dibromo-1,3,5-trimethyl-	15.51	196.99606	854581173
Phenol, 2,4,6-tribromo-	16.49	329.77087	637209104
Phthalic acid, 6-ethyl-3-octyl butyl ester	18.26	149.02339	1402969802

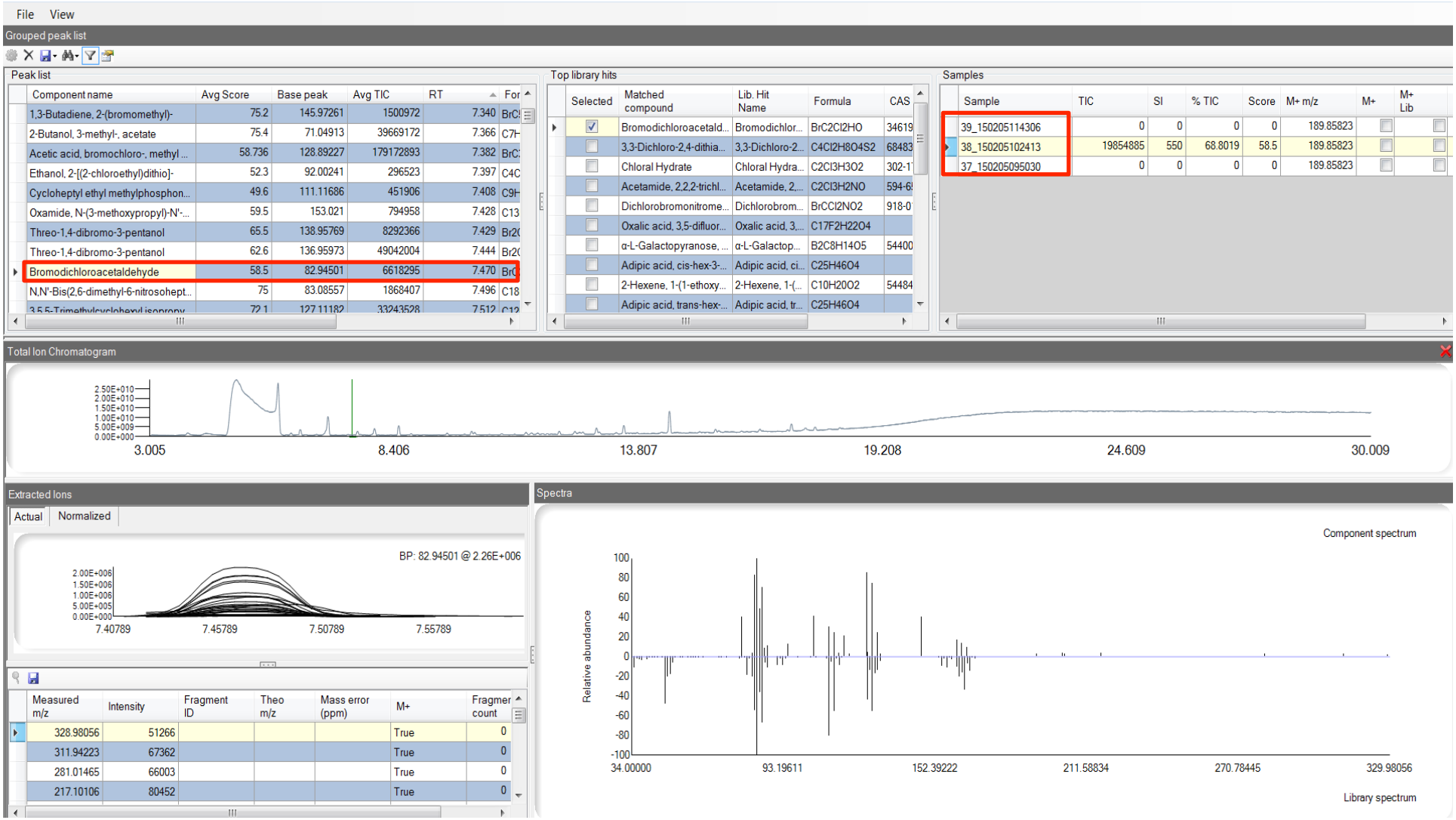
Example of compounds found in sample NL10 DIAZO NH2CL (NIST ID)

23 unique compounds identified in the treated sample compared to blank

Component Name	RT	m/z	Area
Methane, bromo-	3.81893	93.94133	2.59E+09
Methane, iodo-	4.18849	141.9274	1.01E+09
Methane, bromo-	6.12199	93.94133	3.83E+08
Propanoic acid, ethyl ester	6.30544	74.03629	1.3E+09
Methane, dibromo-	6.40918	92.93354	24929829
2-Pentyne, 4,4-dimethyl-	6.41953	81.06994	2.54E+08
Chloroiodomethane	6.61803	175.8884	1.22E+08
2-Pentyne, 4,4-dimethyl-	6.81009	81.06994	13107733
Propanoic acid, 2-methyl-	7.09094	88.05194	68333595
Methane, dibromo-	7.57956	92.93354	5.45E+08
Acetonitrile, dibromo-	8.77223	117.9288	1.31E+08
Ethyl iodoacetate	9.56759	185.9173	3.22E+08
Methyl sorbate	10.90216	95.0492	4954951
Benzene, 1-bromo-2,3-dimethyl-	11.43655	105.07	75604516
Benzoic acid	11.52464	105.0336	4.08E+08
Methane, bromodiiodo-	11.69547	218.8301	1.06E+08
Benzene, 1-(1,1-dimethylethyl)-4-ethoxy-	11.76807	151.1118	12353169
Benzene, 2-bromo-1,3,5-trimethyl-	12.57058	119.0857	51473818
2,6-Diisopropylanisole	13.06213	119.0857	14988011
Benzene, 2-bromo-4-methyl-1-(1-methylethyl)-	13.62064	196.9961	72300603
Phenol, 2,4-dibromo-	13.7705	251.8604	1.61E+08
Benzene, 3-bromo-1,2,4,5-tetramethyl-	14.65367	133.1012	98075372
2,4-Di-tert-butylphenol	14.70524	191.143	80705238

Direct data comparison

Presence/absence of a chromatographic peak in all the sample analysed with abundance information



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Quantification of environmental contaminants: NDMA

Experimental

- Data was acquired at 60,000 resolution (FWHM @ *m/z* 200).
- GC column: TG-200 ms, 30m x 0.25 mm x 0.25 µm
- TraceFinder software for automated data acquisition and processing.

TRACE 1310 GC Parameters	
Injection Volume (µL):	1.0
Liner	Single gooseneck carbofrit packed
Inlet (°C):	220
Inlet Module and Mode:	Splitless
Oven Temperature Program:	
Temperature 1 (°C):	35
Hold Time (min):	1
Temperature 2 (°C):	130
Rate (°C/min)	25
Temperature 3 (°C):	230
Rate (°C/min)	125
Hold Time (min):	1

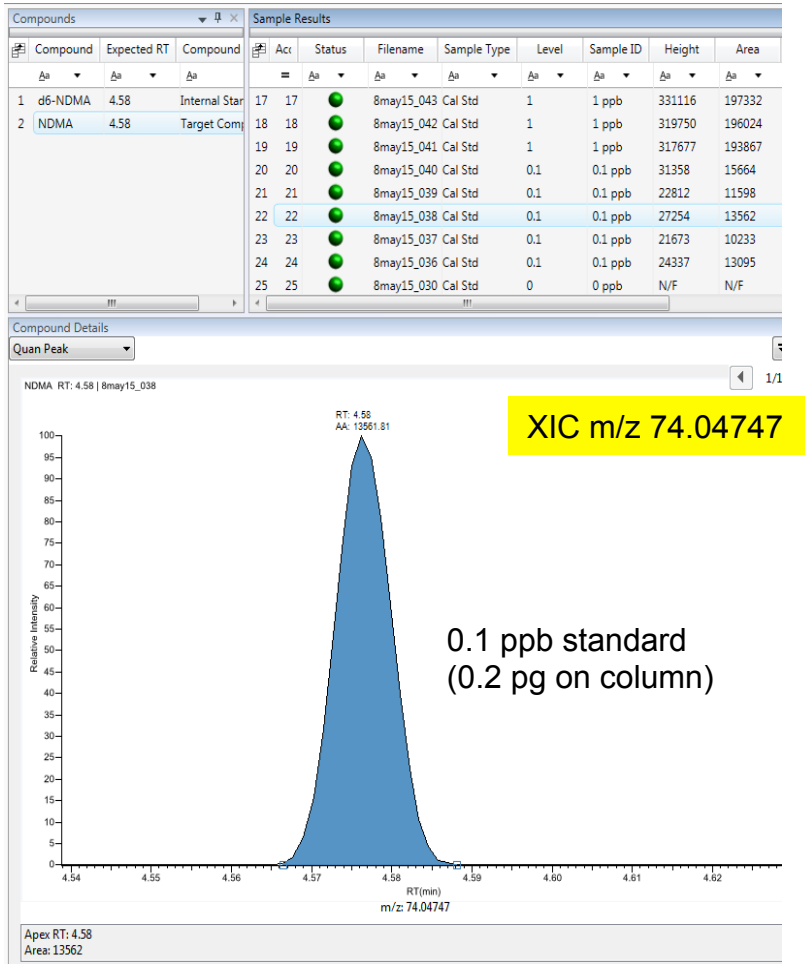
Mass Spectrometer Parameters	
Transfer line (°C):	260
Ionization type:	EI
Ion source(°C):	230
Electron energy (eV):	70
Acquisition Mode:	Full Scan & SIM
Mass range (*m/z*):	50-750
Lockmass (*m/z*):	207.03235

Samples

- Solvent standards (in dichloromethane) each spiked with 20 pg/µL (ppb) d6-NDMA:
  - 0 ppb
  - 0.01 ppb
  - 0.1 ppb
  - 1 ppb
  - 10 ppb
  - 100 ppb

Chromatography @ 0.1 ppb level

Full scan



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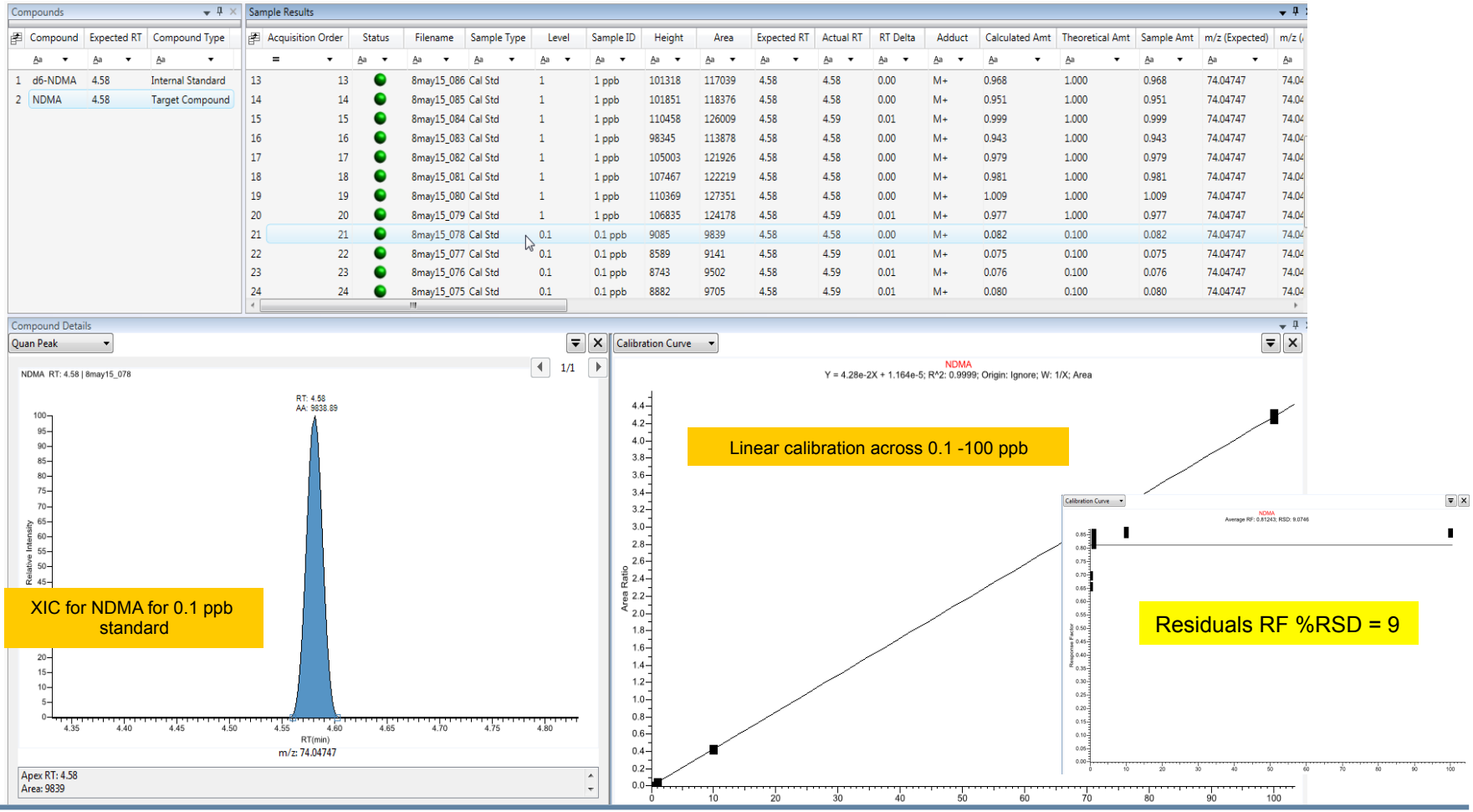
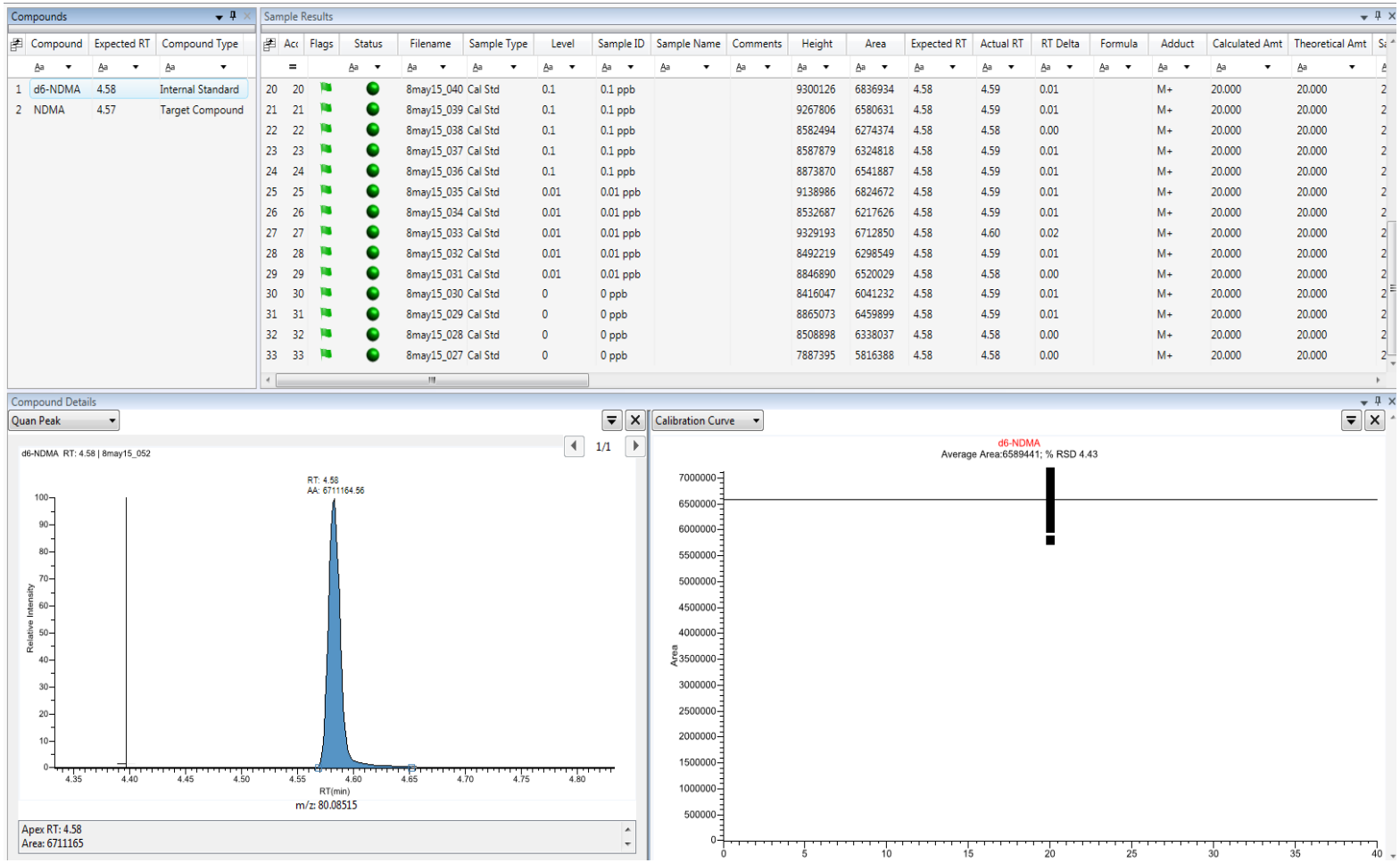
TraceFinder browser
Linearity: 0.1 – 100 ppb

- Linearity was assessed across 0.1 – 100 ppb. d6-NDMA used as internal standard.
- Residuals RF %RSD is also shown (bottom right)



Internal standard (d6-NDMA)
Repeatability of peak area response

- Calculated d6-NDMA peak area %RSD for **n = 33** injections: **4.4%**



Compounds

	Compound	Expected RT	Compound Type
1	d6-NDMA	4.58	Internal Standard
2	NDMA	4.57	Target Compound

Sample Results

	Acc	Flags	Status	Filename	Sample Type	Level	Sample ID	Sample Name	Comments	Height	Area	Expected RT	Actual RT	RT Delta	Formula	Adduct	Calculated Amt	Theoretical Amt
20	20			8may15_040	Cal Std	0.1	0.1 ppb			9300126	6836934	4.58	4.59	0.01		M+	20.000	20.000
21	21			8may15_039	Cal Std	0.1	0.1 ppb			9267806	6580631	4.58	4.59	0.01		M+	20.000	20.000
22	22			8may15_038	Cal Std	0.1	0.1 ppb			8582494	6274374	4.58	4.58	0.00		M+	20.000	20.000
23	23			8may15_037	Cal Std	0.1	0.1 ppb			8587879	6324818	4.58	4.59	0.01		M+	20.000	20.000
24	24			8may15_036	Cal Std	0.1	0.1 ppb			8873870	6541887	4.58	4.59	0.01		M+	20.000	20.000
25	25			8may15_035	Cal Std	0.01	0.01 ppb			9138986	6824672	4.58	4.59	0.01		M+	20.000	20.000
26	26			8may15_034	Cal Std	0.01	0.01 ppb			8532687	6217626	4.58	4.59	0.01		M+	20.000	20.000
27	27			8may15_033	Cal Std	0.01	0.01 ppb			9329193	6712850	4.58	4.60	0.02		M+	20.000	20.000
28	28			8may15_032	Cal Std	0.01	0.01 ppb			8492219	6298549	4.58	4.59	0.01		M+	20.000	20.000
29	29			8may15_031	Cal Std	0.01	0.01 ppb			8846890	6520029	4.58	4.58	0.00		M+	20.000	20.000
30	30			8may15_030	Cal Std	0	0 ppb			8416047	6041232	4.58	4.59	0.01		M+	20.000	20.000
31	31			8may15_029	Cal Std	0	0 ppb			8865073	6459899	4.58	4.59	0.01		M+	20.000	20.000
32	32			8may15_028	Cal Std	0	0 ppb			8508898	6338037	4.58	4.58	0.00		M+	20.000	20.000
33	33			8may15_027	Cal Std	0	0 ppb			7887395	5816388	4.58	4.58	0.00		M+	20.000	20.000

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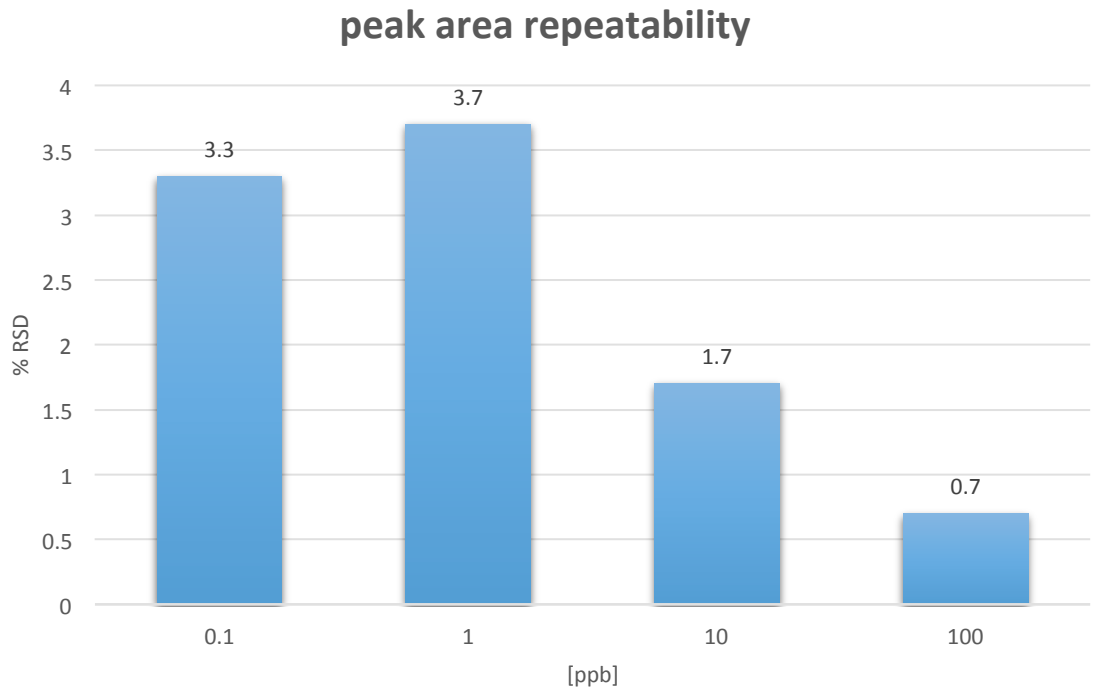
Peak area repeatability

- No manual adjustment of peak integration was used.



** n=5 injections per calibration standard were used except 1.0 ppb level; where n=9 inj. were used*

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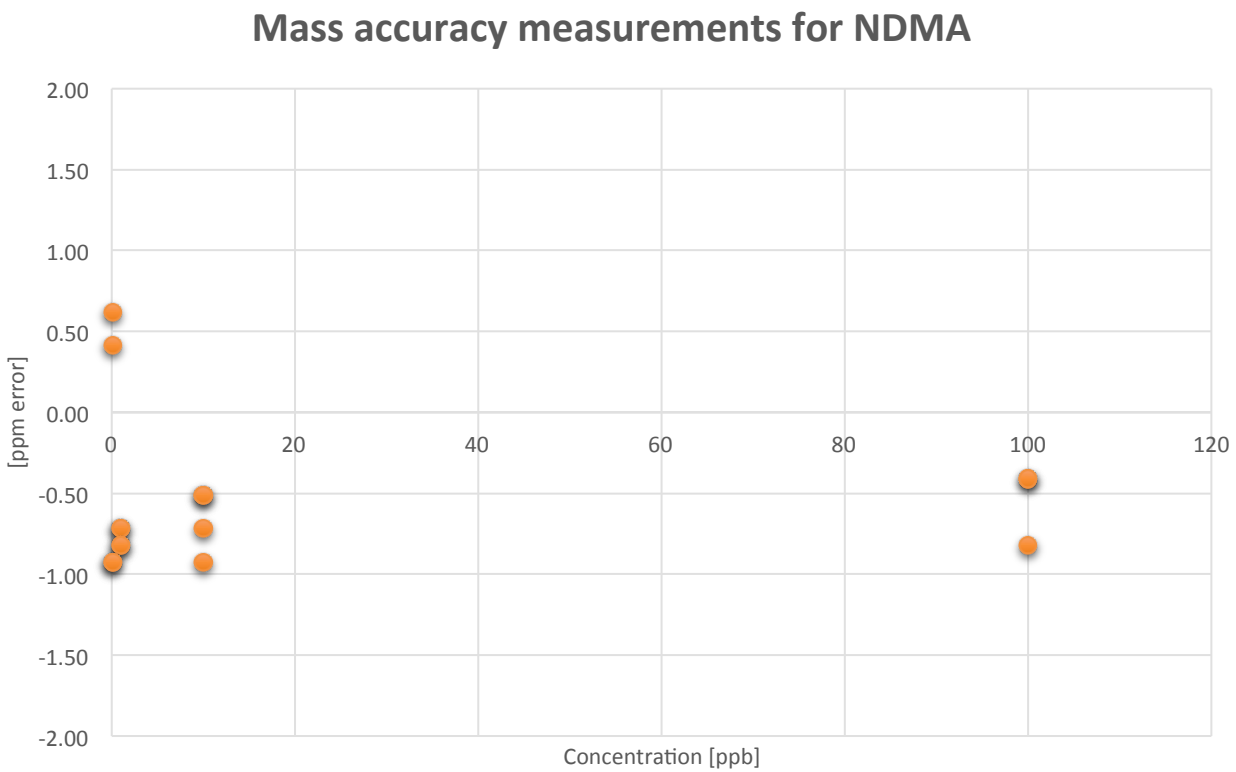
SIM data
Mass accuracy measurements for m/z 74.04747 (NDMA ion)

- Mass error [ppm] across concentration range. Each dot represent a single injection.
- NDMA exact mass: m/z 74.04747.



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Thermo Scientific Q Exactive GC
Hybrid Quadrupole-Orbitrap GC-MS/MS System

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