Traitement de données haute résolution
Etalonnage et masses exactes - Exploitation

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Outlook

How to obtain a mass spectrum as representative as possible of the studied sample?

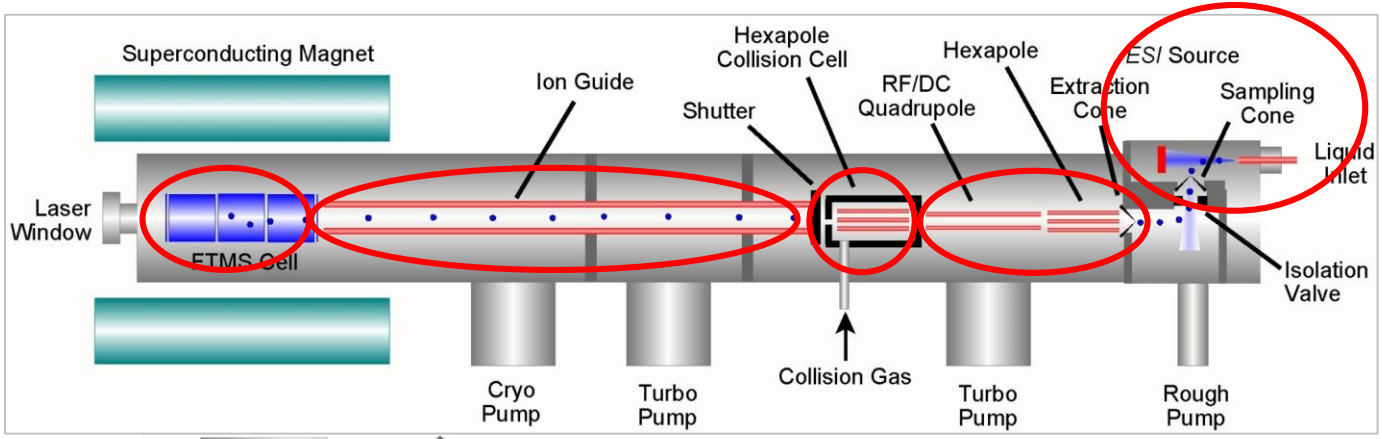
How to obtain a mass spectrum with a good mass measurement accuracy (recalibration methods)?

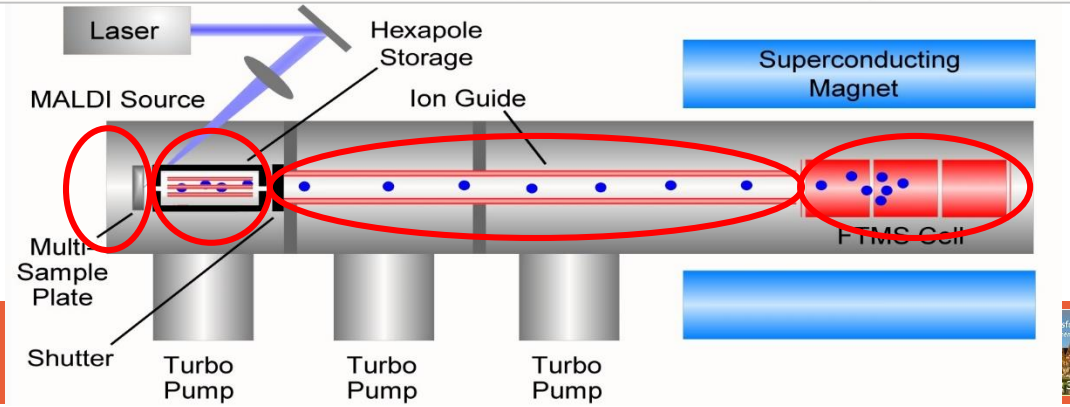
Assignment of the obtained features: from manual to automatized assignment

How to efficiency visualize the data?

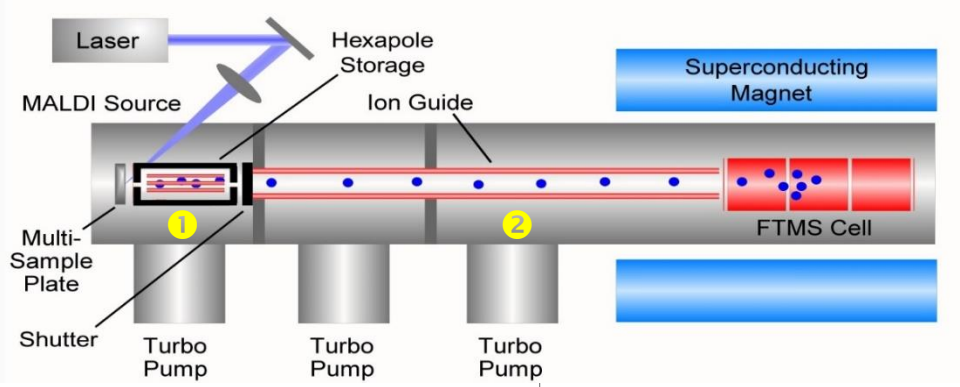
Some examples

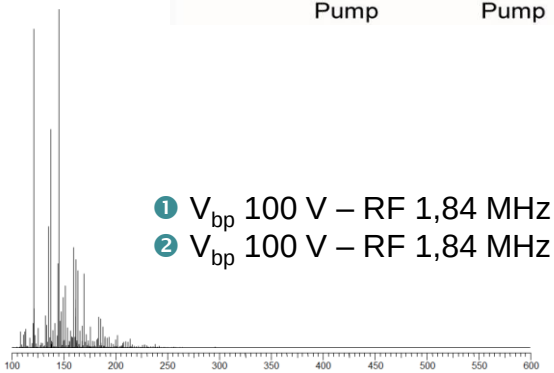
To obtain representative features may a an issue with external ion source



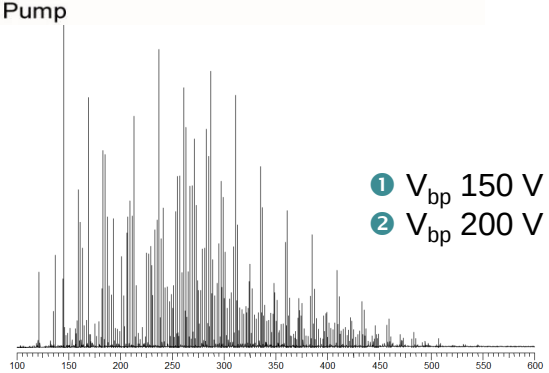


Discrimination coming from the ion transfer





❶ V_{bp} 100 V – RF 1,84 MHz
❷ V_{bp} 100 V – RF 1,84 MHz



❶ V_{bp} 150 V – RF 1,84 MHz
❷ V_{bp} 200 V – RF 1,84 MHz

The accuracy m/z measurement

The fundamental equation in FT-ICR MS

- The m/z ratio is calculated from the cyclotronic frequency
  - In the simplest case, only the value of the magnetic field is considered:

$$\omega_c = z.e.B_0/m$$

  - A more accurate equation takes into account the reduction of ω_c relative to the application of the trapping electric field:

$$\omega_o = \omega c - 2\alpha V_T/a^2 B_0$$

α	Parameter depend of the ICR cell geometry
V_T	Trapping voltage
A	Distance between the trapping plates

The accuracy m/z measurement

Space charge effects (FT-ICR MS)

- Space charge effects come from the electric fields generated by the ions themselves in the ICR cell:
  - 10^6 ions the in the cell lead to the “decrease” of the trapping voltage by 0.05V.
  - A more global equation has to consider the effect of the magnetic field, the trapping potential and the space charges:

$$\omega_o = \omega_c - 2\alpha V_T/a^2 B_0 - q\rho G_i/\varepsilon_o B_0$$

q Charge

ρ Charge density

G_i Geometric parameter linked to the shape of the ion clouds

Masselon, Tolmachev, Anderson, Harkewicz, Smith *JASMS 2002; 13: 99-106.*

The accuracy m/z measurement

Calibration of FT-ICR MS

- For an optimum m/z measurement accuracy, the trapping voltage, the magnetic field, the number of ions have to be as constant as possible (the charge density ρ has to be as low as possible: highly diluted case or total ion current has to be taken into account).

$$\omega_o = \omega_c - 2\alpha V_T/a^2 B_0 - q\rho G_i/\varepsilon_o B_0$$

Constant

$2\pi f$ $\quad qB_0/m \equiv A/(m/z)$ $\quad B$

- Finally

$$f = K_1/(m/z) + K_2$$

Calibration and recalibration – FT-ICR MS

– Diluted medium

$$f = \frac{K_1}{m/z} + K_2 \qquad m/z = \frac{K_1}{f - K_2} \qquad m/z = \frac{A}{f} + \frac{B}{f^2}$$

– Correction of the charge density for the i ions

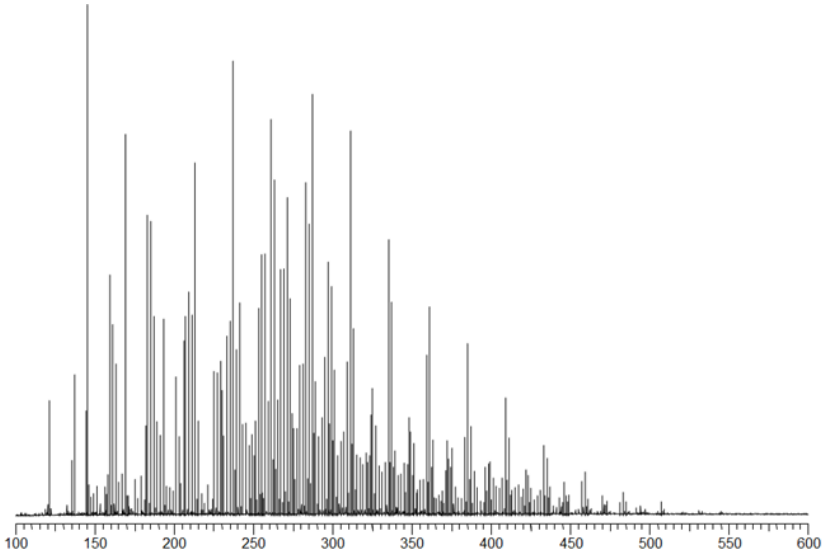
$$f = \frac{K_1}{m/z} + K_2 + K_3 I_i \qquad m/z = \frac{K_1}{f - K_2 - K_3 I_i} \qquad m/z = \frac{A}{f} + \frac{B + CI_i}{f^2}$$

– For average mass spectrum additional correction to take into account the variation of the total ion current

$$f = \frac{K_1}{m/z} + K_2 + K_3 I_i + K_4 I_{tot} \qquad m/z = \frac{K_1}{f - K_2 - K_3 I_i - K_4 I_{tot}} \qquad m/z = \frac{A}{f} + \frac{B + CI_i + DI_{tot}}{f^2}$$

Calibration and recalibration – FT-ICR MS

Results



	$m/z = \frac{A}{f} + \frac{B}{f^2}$	$m/z = \frac{A}{f} + \frac{B + CI_i}{f^2}$
Average	0,72 ppm	0,69 ppm
P_{25}	0,34 ppm	0,33 ppm
P_{50}	0,65 ppm	0,62 ppm
P_{75}	1,02 ppm	0,98 ppm
Σ_{error}	0,015 ppm	0,008 ppm

The accuracy m/z measurement – Calibration

Equation de Calibration en Orbitrap

- Highly diluted medium (simplest equation)

$$m/z = \frac{B}{f^2}$$

- Space charge effect created by an amount of Q charges

$$m/z = \frac{B(Q)}{f^2}$$

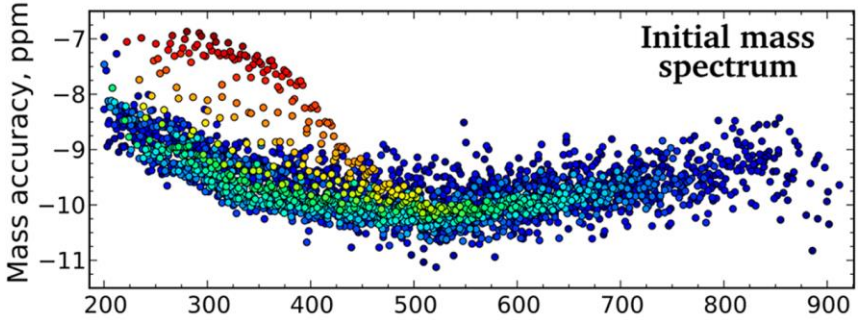
- To refine the consideration of the space charge effect an additional parameter may be used

$$m/z = \frac{B(Q)}{f^2} + \frac{C(Q)}{f^3}$$

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Orbitrap

Exemple



- The error is depending on the m/z ratio and the ion abundance
- How to proceed
  - Define internal calibrant ions
  - Determine the ε error function for these calibrants

$$\varepsilon_j = \varepsilon\left(\left(m/z\right)_j; A_j\right) = \frac{\left(m/z\right)_{obs,j} - \left(m/z\right)_j}{\left(m/z\right)_j}$$

  - Increase the m/z measurment accurancy by minimization of the ε_j

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Recalibration

- For n calibrant ions, the minimization of ε_j leads to the error function which weights each error by ω_j

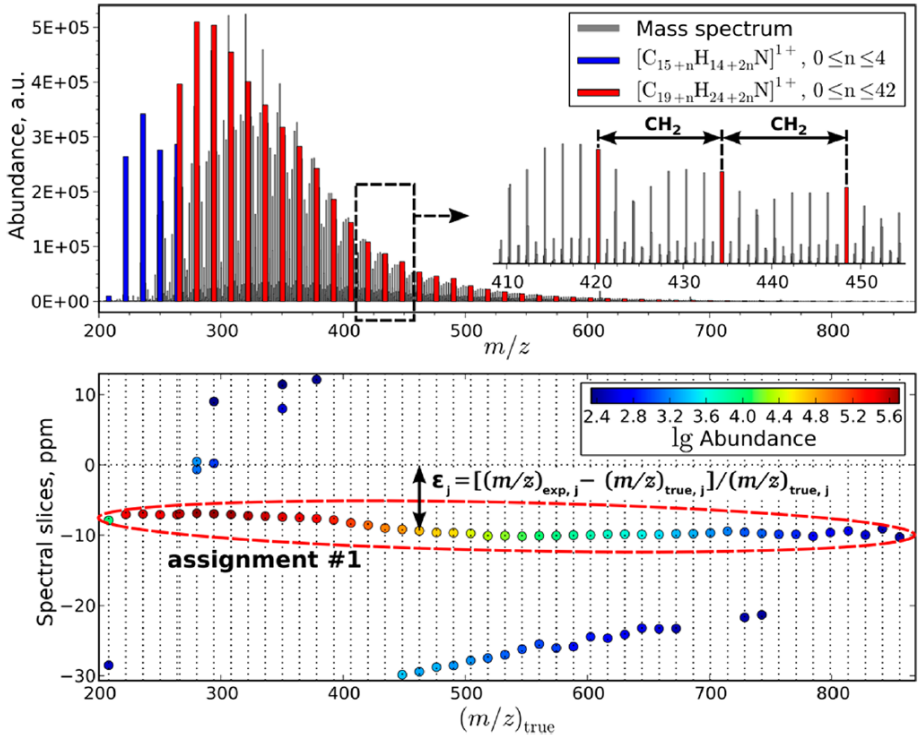
$$\varepsilon(m/z) = \sum_{j=1}^{n} \omega_j \varepsilon_j$$

- The estimation of the error function is done by a binomial approach
- The global mass spectrum is divided in n – 1 intervals (n calibrants) to define the abundance error function.
- The m/z and A (abundance) variables are splitted

$$\varepsilon_j\left((m/z); A\right) = \varepsilon_j(m/z) + \varepsilon_j(A)$$

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

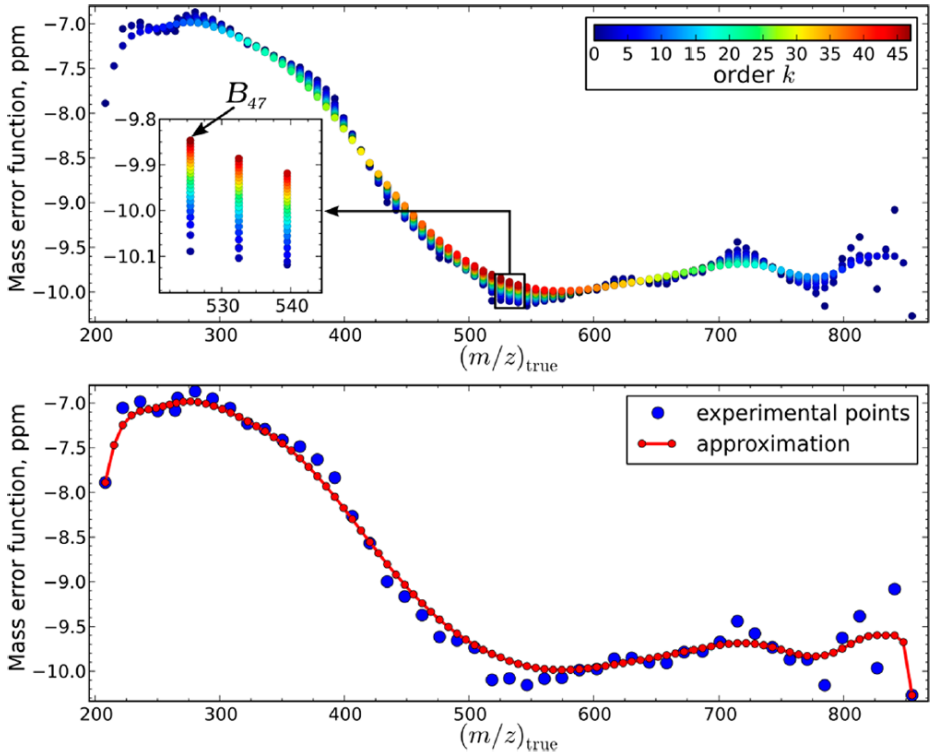
The accuracy m/z measurement – Recalibration



48 calibrants
208,1 <m/z< 854,8

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Recalibration

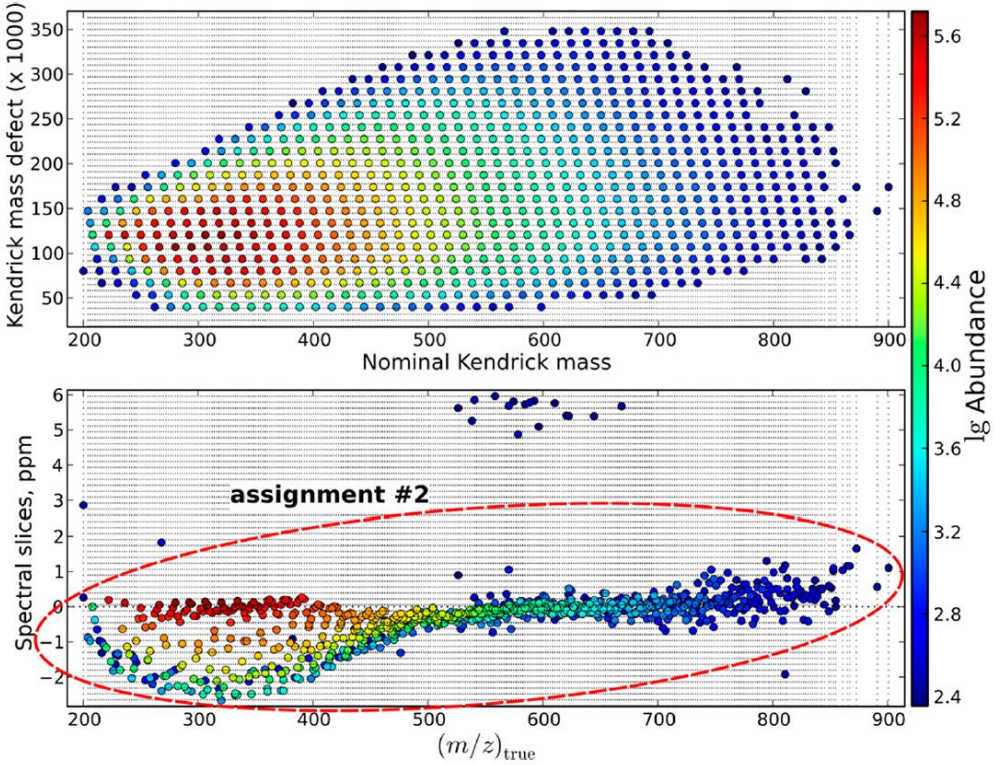


Determination of

$$\varepsilon(m/z)$$

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Recalibration

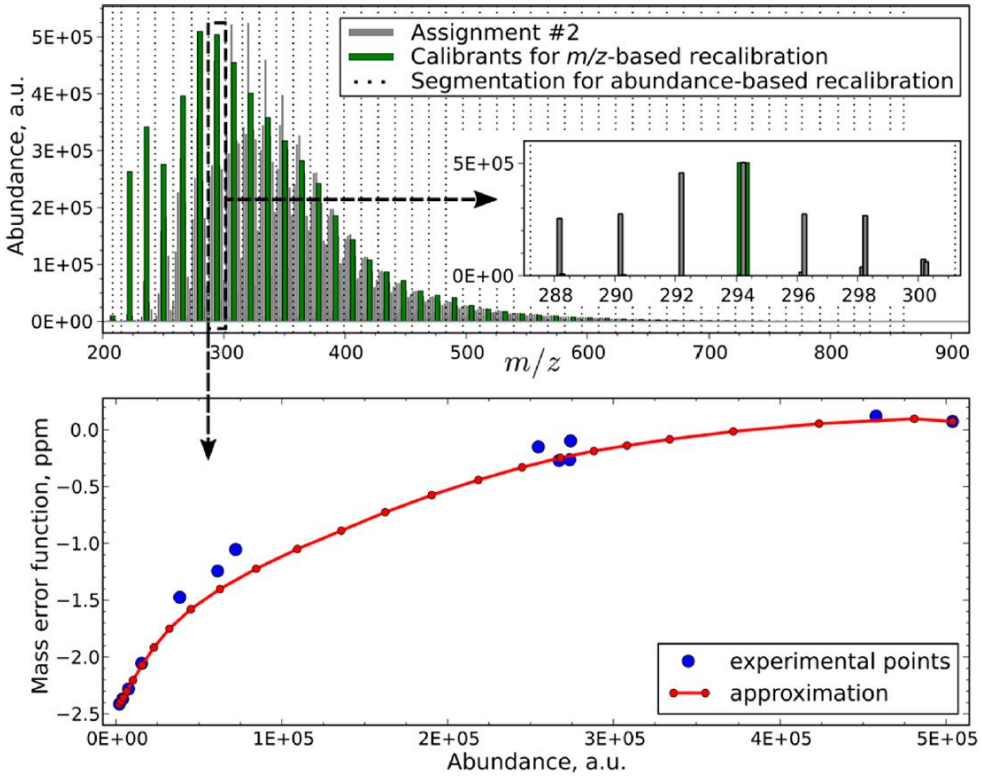


Validation by considering the distribution of one class of compounds (the 843 signals relative to C_xH_yN species)

Reassignment

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Recalibration

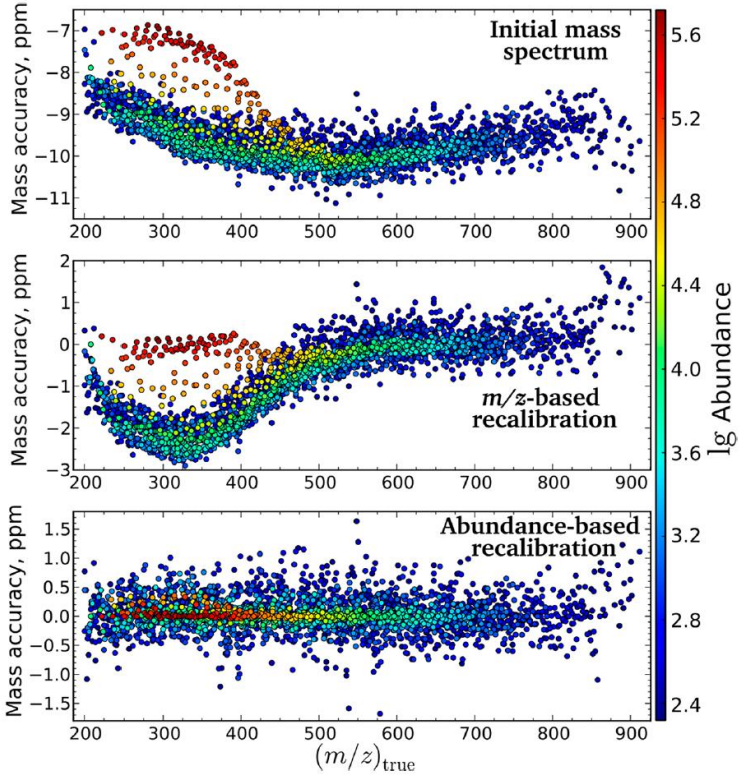


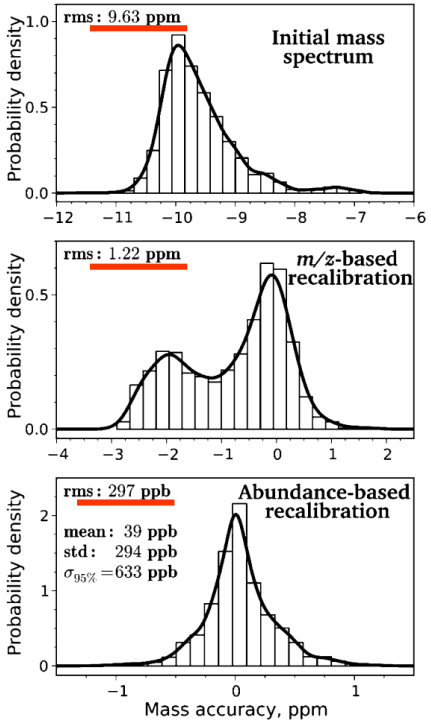
Determination of

$\varepsilon(A)$

Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

The accuracy m/z measurement – Recalibration





Kozhinov, Zhurov, Tsybin *Anal Chem 2013; 85: 6037-6445.*

Assignment

Assignment by the only use of the accurate m/z measurement

Elemental Composition Search Report:

Target Mass:
Target m/z = 285.04015 ± 2.00ppm
Charge = -1

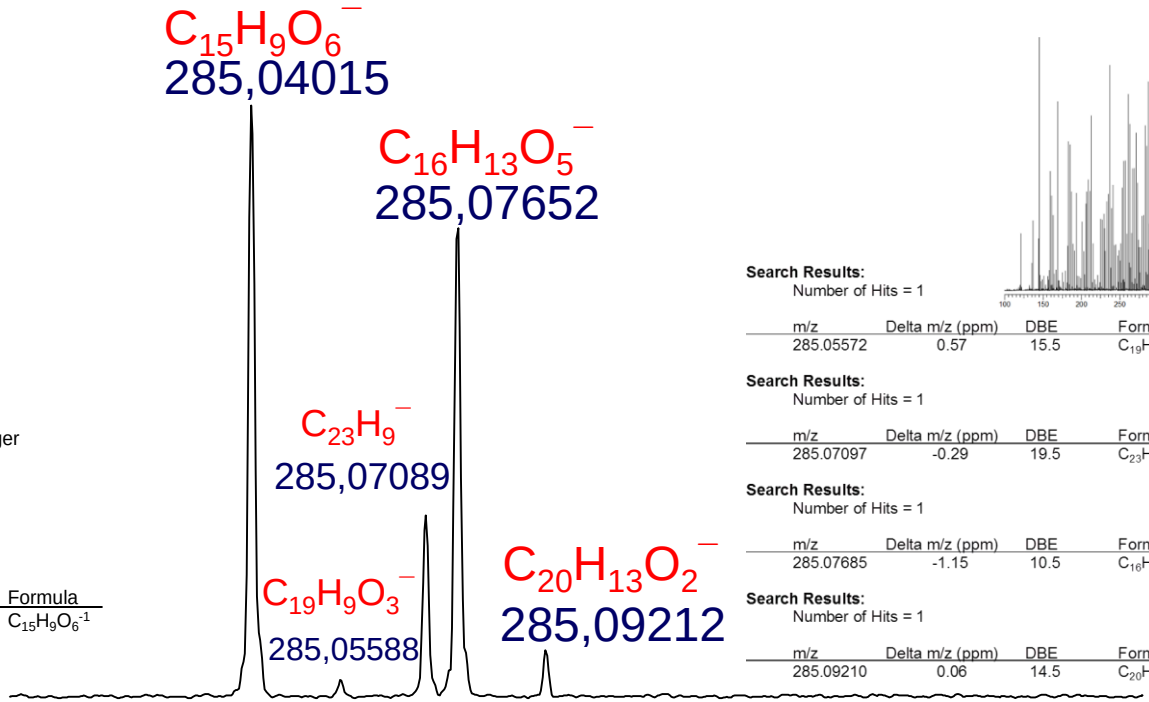
Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
N	14.003074	0	1
O	15.994915	0	100
S	31.972071	0	1

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
-Minimum DBE = 0
-Maximum DBE = 100

Search Results:
Number of Hits = 1

m/z	Delta m/z (ppm)	DBE	Formula
285.04046	-1.10	11.5	$C_{15}H_9O_6^{-1}$



Search Results:
Number of Hits = 1

m/z	Delta m/z (ppm)	DBE	Formula
285.05572	0.57	15.5	$C_{19}H_9O_3^{-1}$

Search Results:
Number of Hits = 1

m/z	Delta m/z (ppm)	DBE	Formula
285.07097	-0.29	19.5	$C_{23}H_9^{-1}$

Search Results:
Number of Hits = 1

m/z	Delta m/z (ppm)	DBE	Formula
285.07685	-1.15	10.5	$C_{16}H_{13}O_5^{-1}$

Search Results:
Number of Hits = 1

m/z	Delta m/z (ppm)	DBE	Formula
285.09210	0.06	14.5	$C_{20}H_{13}O_2^{-1}$

The double bond equivalent (DBE)

Determination of the number of unsaturation (double bond and ring)

$$DBE = 1 + \frac{\sum_{i}^{i_{max}} N_i (V_i - 2)}{2}$$

- N_i : Number of atom i
- V_i : Valence of the atom i

For the “classical” atoms

$$DBE = 1 + \frac{1}{2}(2C + 2Si - H - F - Cl - Br - I + N + P)$$

Bivalent atoms (oxygen, …) have no effect on the DBE value

Integer DBE value: radical ion

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

The six golden rules for the ion assignment

The Seven Golden Rules use heuristic rules for limiting the number of formulas only to the most probable ones

1. In respect with the measured m/z, limitation of the number of atoms for a given chemical element (databases)

Table 1: Restrictions for number of elements during formula generation for small molecules based on examination of the DNP and Wiley mass spectral databases. For each element, the higher count was taken for denominating the element restriction rule #1

Mass Range [Da]	Library	C max	H max	N max	O max	P max	S max	F max	Cl max	Br max	Si max
< 500	DNP	29	72	10	18	4	7	15	8	5	
	Wiley	39	72	20	20	9	10	16	10	4	8
< 1000	DNP	66	126	25	27	6	8	16	11	8	
	Wiley	78	126	20	27	9	14	34	12	8	14
< 2000	DNP	115	236	32	63	6	8	16	11	8	
	Wiley	156	180	20	40	9	14	48	12	10	15
< 3000	DNP	162	208	48	78	6	9	16	11	8	

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

The six golden rules for the ion assignment

2. Respect of the Lewis rules

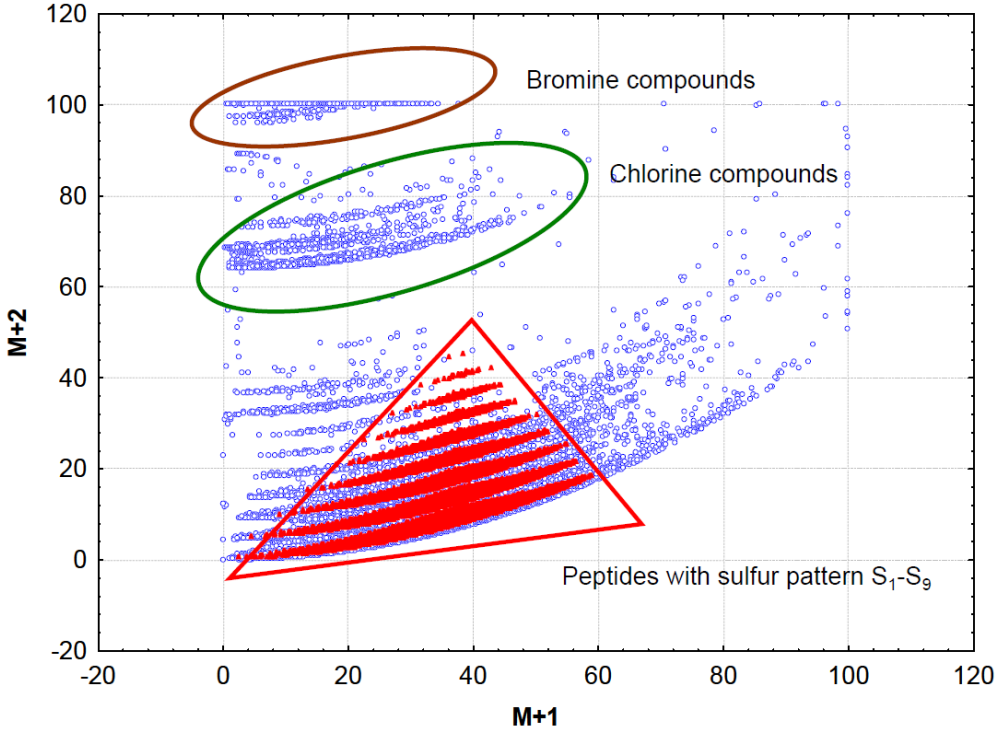
Application of the Lewis rules: valence of the atoms, bonding and non-bonding electrons pairs, octet rule, … (the main part of the program doesn't part of these rules)

3. The isotopic distribution

The relative abundance of M+1 and M+2 contribution are useful to define the number of carbon atoms and the species including sulfur, chlorine or bromine atom

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

The six golden rules for the ion assignment



From the Wiley database
(45 000 compounds)

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

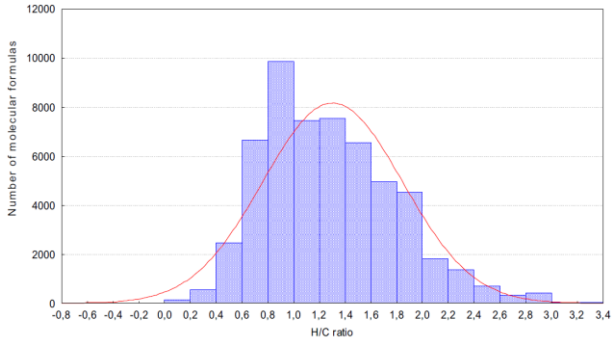
The six golden rules for the ion assignment

4. Hydrogen/Carbon ratio – Value of the DBE

The H/C is ranging between 0 (graphite) and 3 (cf carbone valence)

In some specific cases, it may be higher

4 : methane CH_4 6 : methylhydrazine CH_6N_2



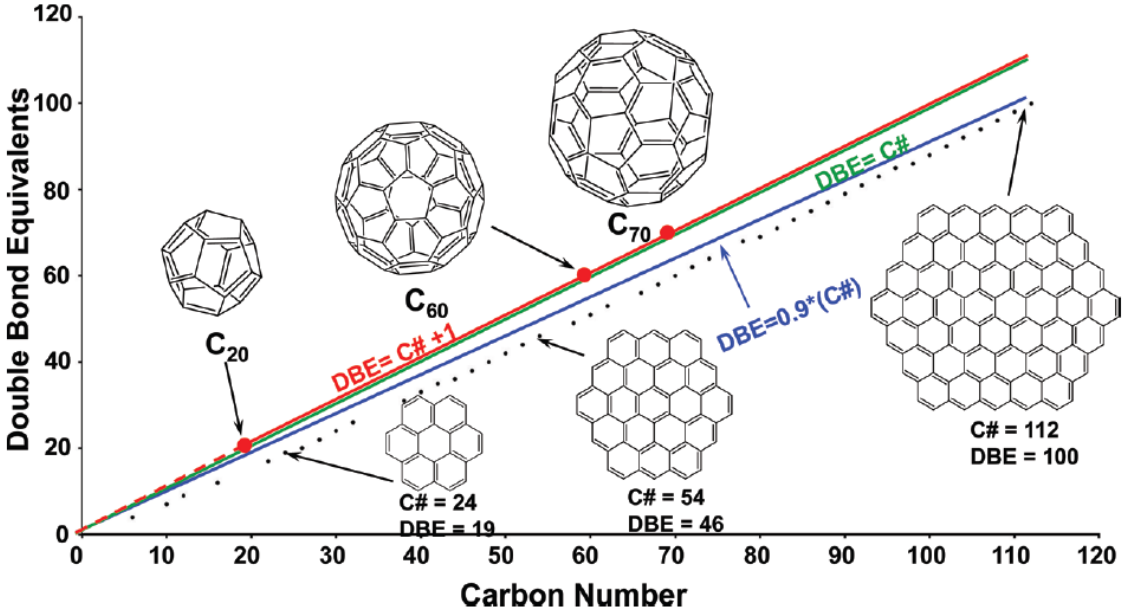
In all cases DBE of the ions ≥ 0 (exception: saturated compounds with adduit (NH_4^+, H^+)

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

Lobodin, Marshall, Hsu *Anal. Chem. 2012; 84: 3410-3416.*

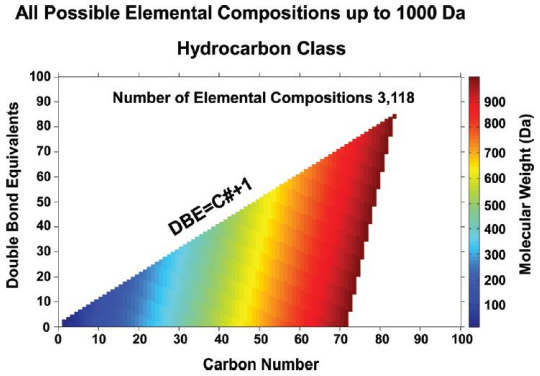
The six golden rules for the ion assignment

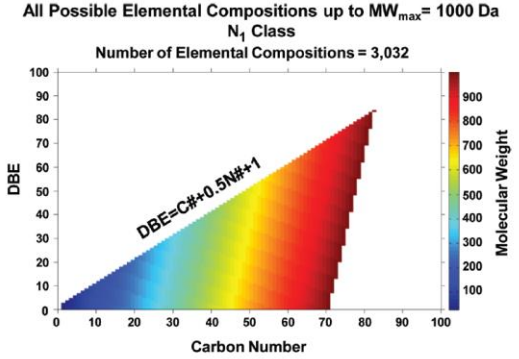
$$DBE = 1 + \frac{1}{2}(2C + 2Si - H - F - Cl - Br - I + N + P)$$

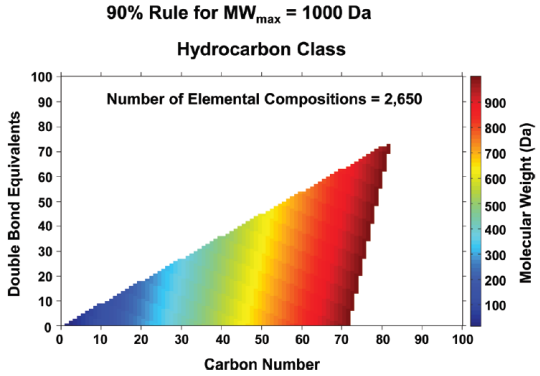


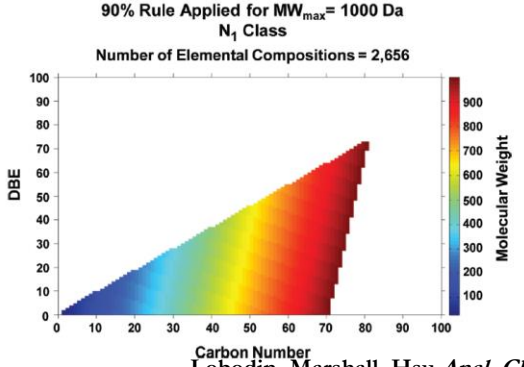
Lobodin, Marshall, Hsu *Anal. Chem. 2012; 84: 3410-3416.*

The six golden rules for the ion assignment









Lobodin, Marshall, Hsu *Anal. Chem. 2012; 84: 3410-3416.*

The six golden rules for the ion assignment

5. Relative distribution of the elements

Define the more probable ratio between two elements (in respect with chemical compound databases)

Table 2: Common element ratios obtained from 45.000 formulas comprising the Wiley mass spectral database for the mass range 30 Da – 1500 Da

Element ratios	Common range (covering 99.7%)	Extended range (covering 99.99%)	Extreme range (beyond 99.99%)
H/C	0.2–3.1	0.1–6	< 0.1 and 6–9
F/C	0–1.5	0–6	> 1.5
Cl/C	0–0.8	0–2	> 0.8
Br/C	0–0.8	0–2	> 0.8
N/C	0–1.3	0–4	> 1.3
O/C	0–1.2	0–3	> 1.2
P/C	0–0.3	0–2	> 0.3
S/C	0–0.8	0–3	> 0.8
Si/C	0–0.5	0–1	> 0.5

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

The six golden rules for the ion assignment

6. Maximum number of heteroatoms

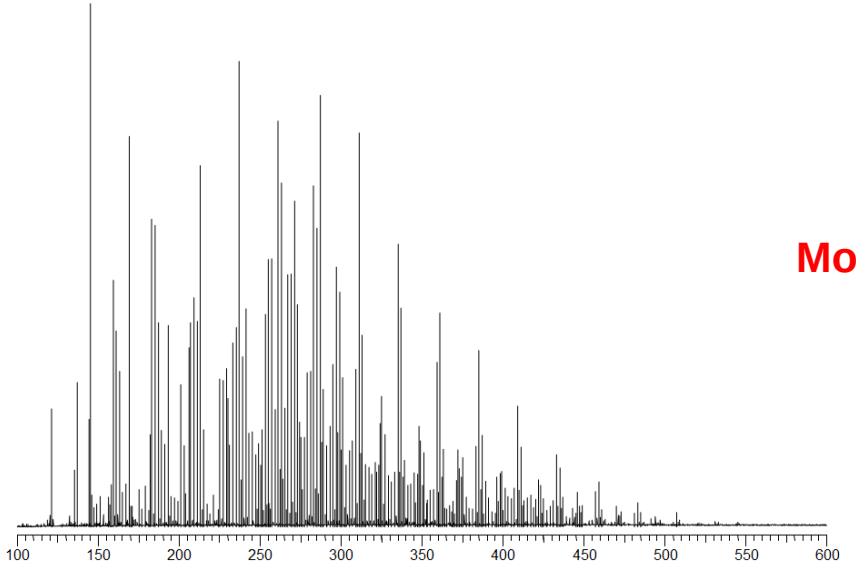
Define the more probable amounts of heteroatoms (N, O, P, S) in respect with the Beilstein chemical compound database

Table 3: Multiple element count restriction for compounds < 2000 Da, based on the examination of the Beilstein database and the Dictionary of Natural Products

Element counts	Heuristic Rule	DB examples for maximum values
NOPS all > 1	N< 10, O < 20, P < 4, S < 3	$C_{15}H_{34}N_9O_8PS$, $C_{22}H_{44}N_4O_{14}P_2S_2$, $C_{24}H_{38}N_7O_{19}P_3S$
NOP all > 3	N < 11, O < 22, P < 6	$C_{20}H_{28}N_{10}O_{21}P_4$, $C_{10}H_{18}N_5O_{20}P_5$
OPS all > 1	O < 14, P < 3, S < 3	$C_{22}H_{44}N_4O_{14}P_2S_2$, $C_{16}H_{36}N_4O_4P_2S_2$
PSN all > 1	P < 3, S < 3, N < 4	$C_{22}H_{44}N_4O_{14}P_2S_2$, $C_{16}H_{36}N_4O_4P_2S_2$
NOS all > 6	N < 19 O < 14 S < 8	$C_{59}H_{64}N_{18}O_{14}S_7$

Kind, Fiehn *BMC Bioinformatics 2007; 8: 105.*

What about the data treatment for non-targeted analysis?



More than 1000 features

- Assign a chemical formulae to each signal (up 100,000 peaks).
- Represent the obtained features to allow comparison.

Assignment of the features

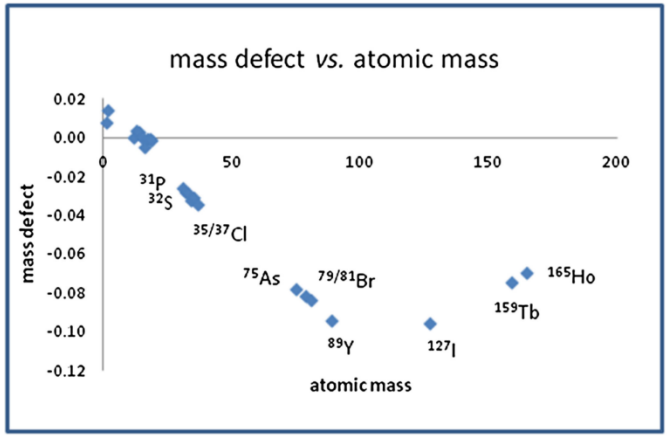
Using the six golden rules and the accurate m/z measurement the assignment of very high resolution data is possible. Nevertheless,

- The number of features is huge (thousands of peaks in petroleomic);
- For high m/z ratio, the accuracy of measurement is not enough for an unambiguous assignment;
- The resolution is not always high enough to distinguish each contribution

	0	6	12	18	34	40
$C_{15}H_{27}(CH_2)_nO_3S_2^+$	319.14071	403.23461	487.32851	571.42241	655.51631	739.61021
$C_{15}H_{19}(CH_2)_nN_4O_4^+$	319.14120	403.23508	487.32898	571.42288	655.51678	739.61068
Δ (ppm)	-1.47	-1.17	-0.96	-0.82	-0.72	-0.64

Alternatives have to be found for automatic and iterative assignment

The use of the mass defect



element	Isotope	atomic mass (u)	mass defect	% isotopic composition
hydrogen	^{1}H	1.00783	0.00783	99.9885
	^{2}H	2.01410	0.01410	0.0115
carbon	^{12}C	12.00000	0.00000	98.93
	^{13}C	13.00335	0.00335	1.07
nitrogen	^{14}N	14.00307	0.00307	99.632
	^{15}N	15.00011	0.00011	0.368
oxygen	^{16}O	15.99491	-0.00509	99.757
	^{17}O	16.99913	-0.00087	0.038
	^{18}O	17.99916	-0.00084	0.205
fluorine	^{19}F	18.99840	-0.00160	100
phosphorus	^{31}P	30.97377	-0.02623	100
sulfur	^{32}S	31.97207	-0.02793	94.93
	^{33}S	32.97146	-0.02854	0.76
	^{34}S	33.96787	-0.03213	4.29
chlorine	^{35}Cl	34.96885	-0.03115	75.78
	^{37}Cl	36.96590	-0.03410	24.22
arsenic	^{75}As	74.92160	-0.07840	100
bromine	^{79}Br	78.91834	-0.08166	50.69
	^{81}Br	80.91629	-0.08371	49.31
yttrium	^{89}Y	88.90585	-0.09415	100
iodine	^{127}I	126.90447	-0.09553	100
terbium	^{159}Tb	158.92534	-0.07466	100
holmium	^{165}Ho	164.93032	-0.06968	100

Sleno *JMS 2012; 47: 226-236.*

The use of the Kendrick mass

The Kendrick Mass (KM)

$$KM = measured\ mass \times \frac{14.00000}{14.01565}$$

14,01565 ≡ mass of a CH_2

Other bases are possible

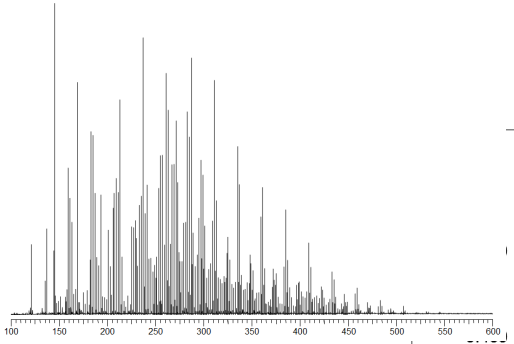
Kendrick mass defect (KMD)

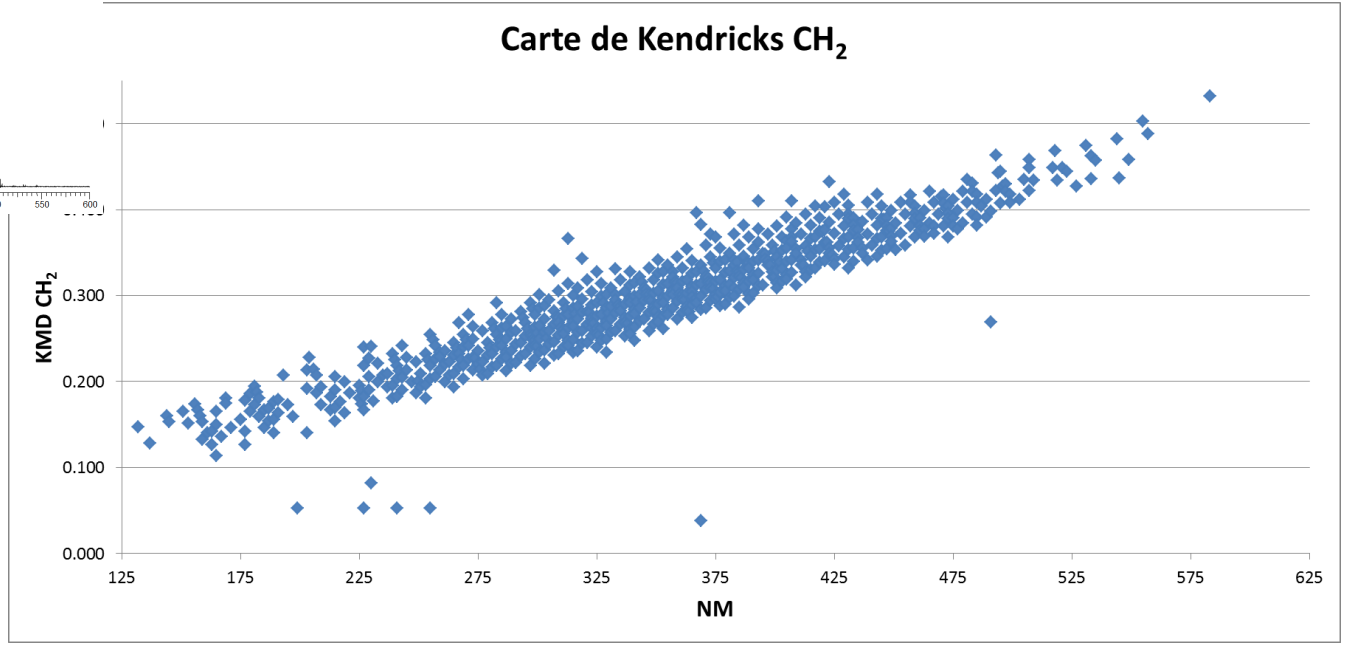
$$KMD = nominal\ mass - KM$$

Advantages

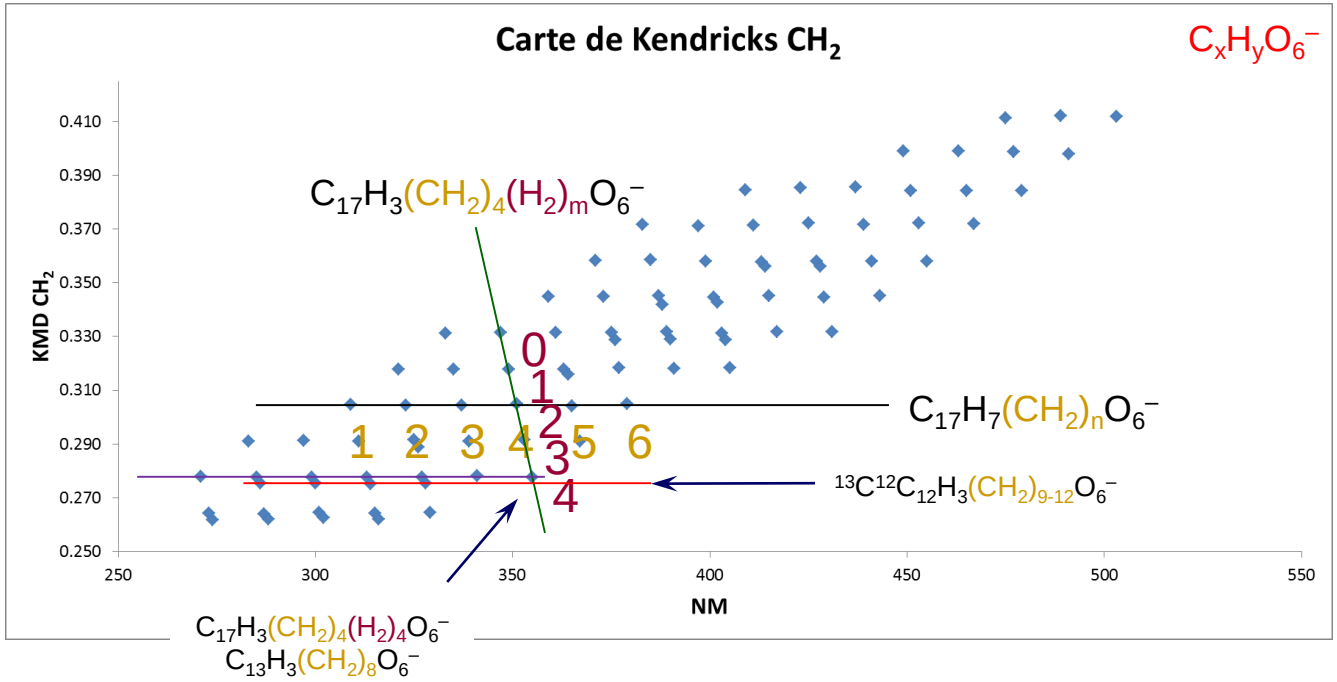
- All the alkylated derivate of a given compound have the same KMD.
- KMD is connected to the number of unsaturation.
- The KM et KMD may be calculated with other repeat units (H_2, O, CH_2O,…)

Use of the Kendrick mass

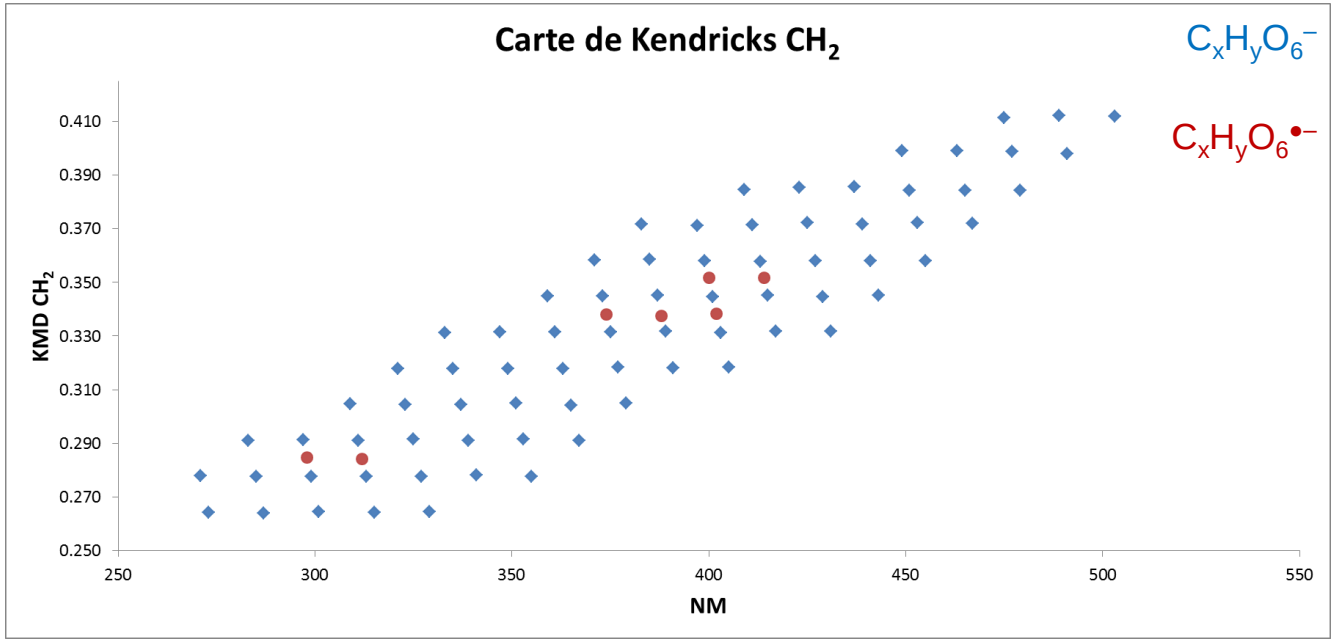




Use of the Kendrick mass

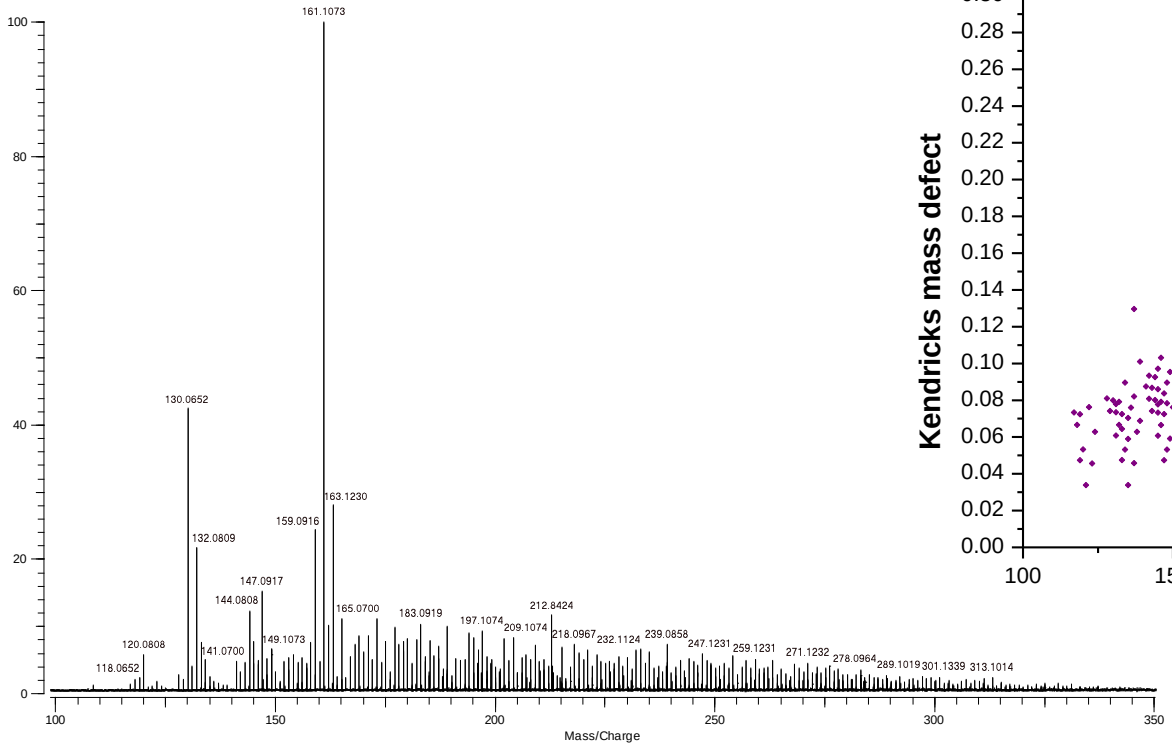


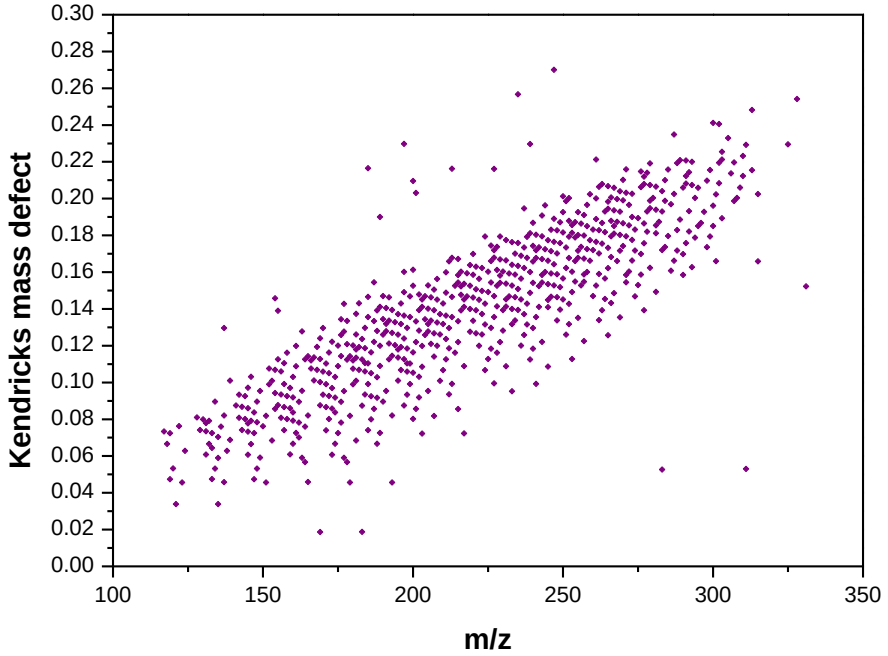
Use of the Kendrick mass



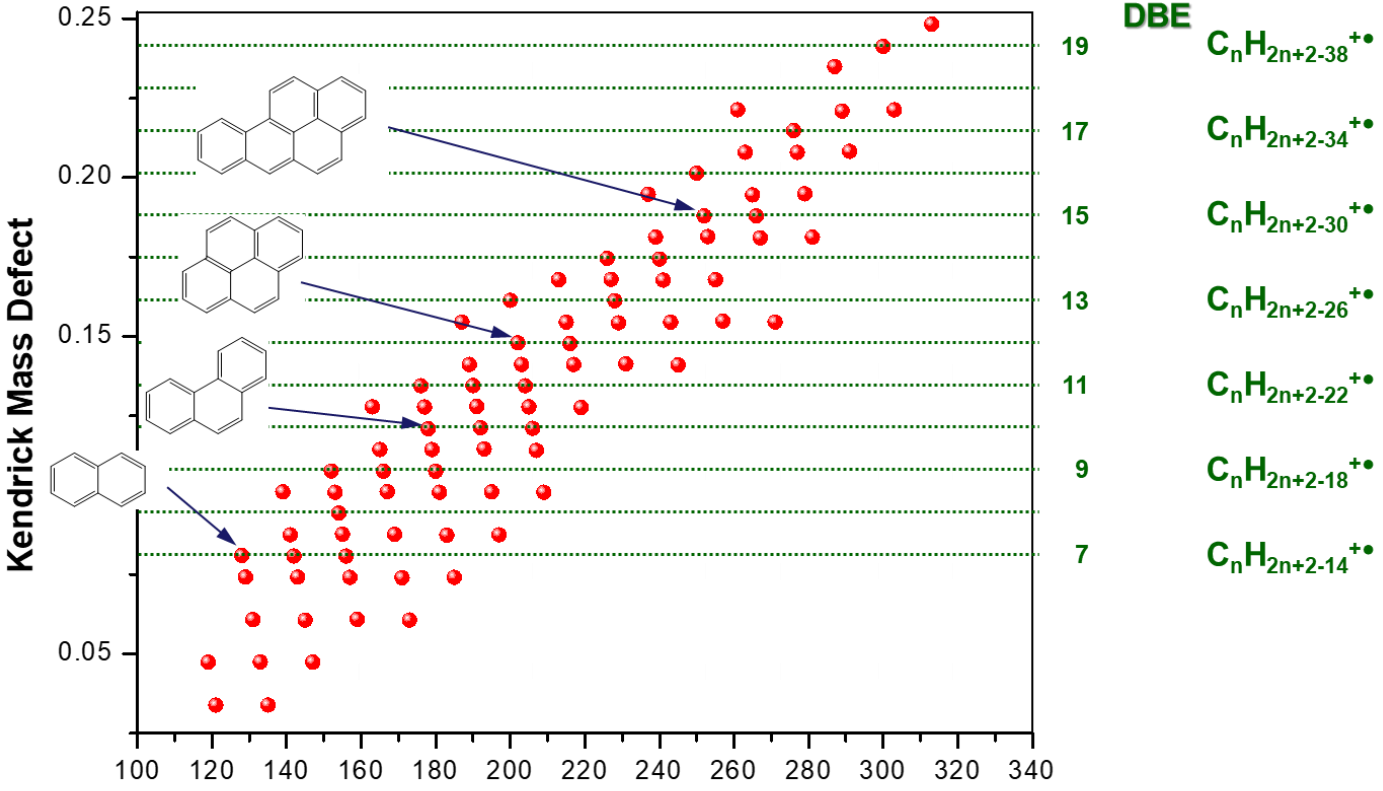
Distinguishing radical cations from cations

Use of the Kendrick mass

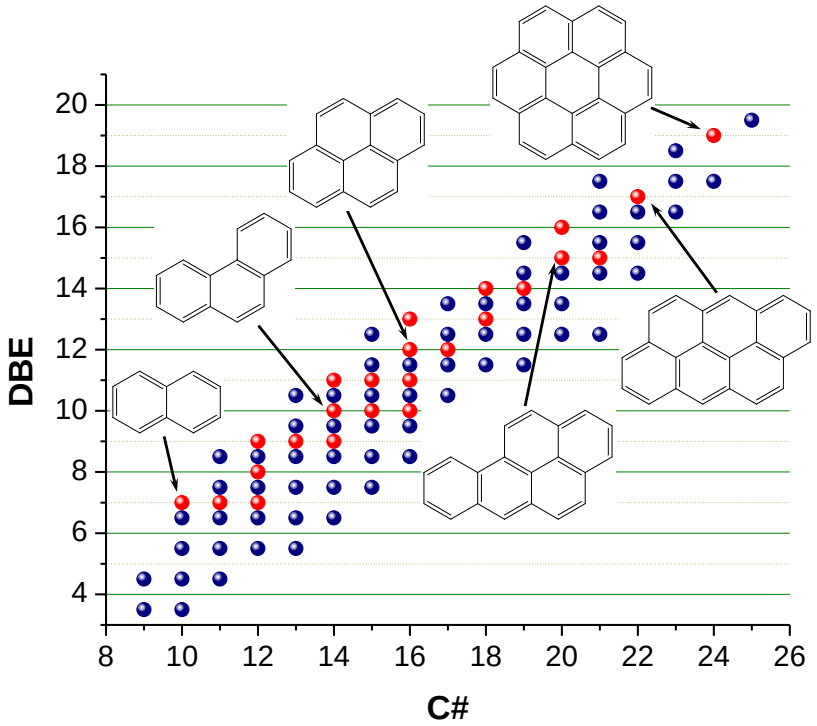




Use of the Kendrick mass



Use of the Kendrick mass



PAHs and **methyl or dimethyl PAHs** : $M^{+\bullet}$

Alkyl PAHs detected as $[M - H]^+$, $[M - CH_3]^+$ or $[M - C_xH_{2x+1}]^+$

Use of the Kendrick mass

The KMD(CH_2) values are tabulated

- for positive and negative ions;
- in respect with the nature and the amounts of heteroatoms;
- the – z value defines the unsaturation level:

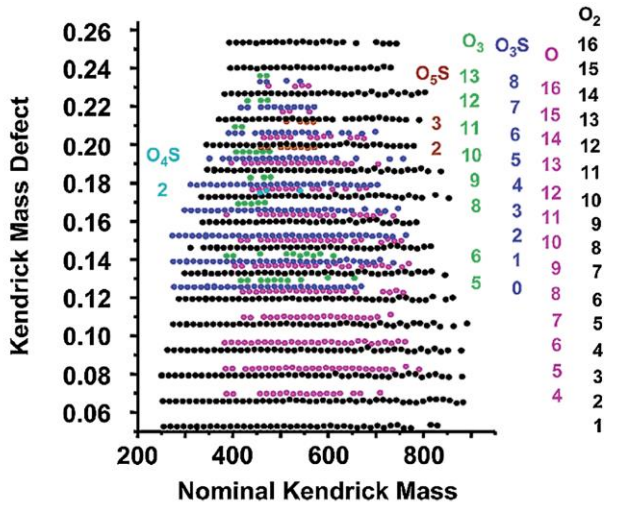
$$C_nH_{2n+z}X$$

  - the – 1 serie is $C_nH_{2n-1}^-$
  - the – 2O serie is $C_nH_{2n-2}O^{\bullet-}$
  - the – $1O_2$ serie is $C_nH_{2n-2}O_2^-$

Negative ions	
KMD	Series
0.01285	-1
0.01955	-2
0.02542	-1N
0.02625	-3
0.03212	-2N
0.03295	-4
0.03580	-1O
0.03882	-3N
0.03965	-5
0.04250	-2O
0.04552	-4N
0.04635	-6
0.04836	-1NO
0.04920	-3O
0.05222	-5N
0.05305	-7
0.05506	-2NO
0.05590	-4O
0.05875	$-1O_2$
0.05892	-6N
0.05975	-8
0.06176	-3NO
0.06260	-5O
0.06544	$-2O_2$

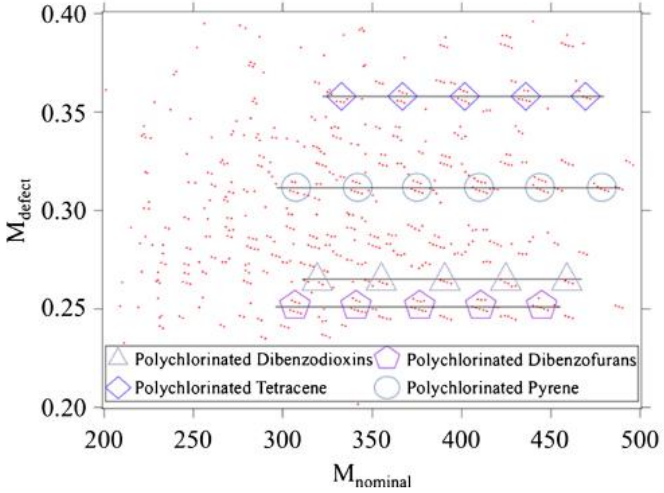
Use of KMD and Mass defect

Petroleomic



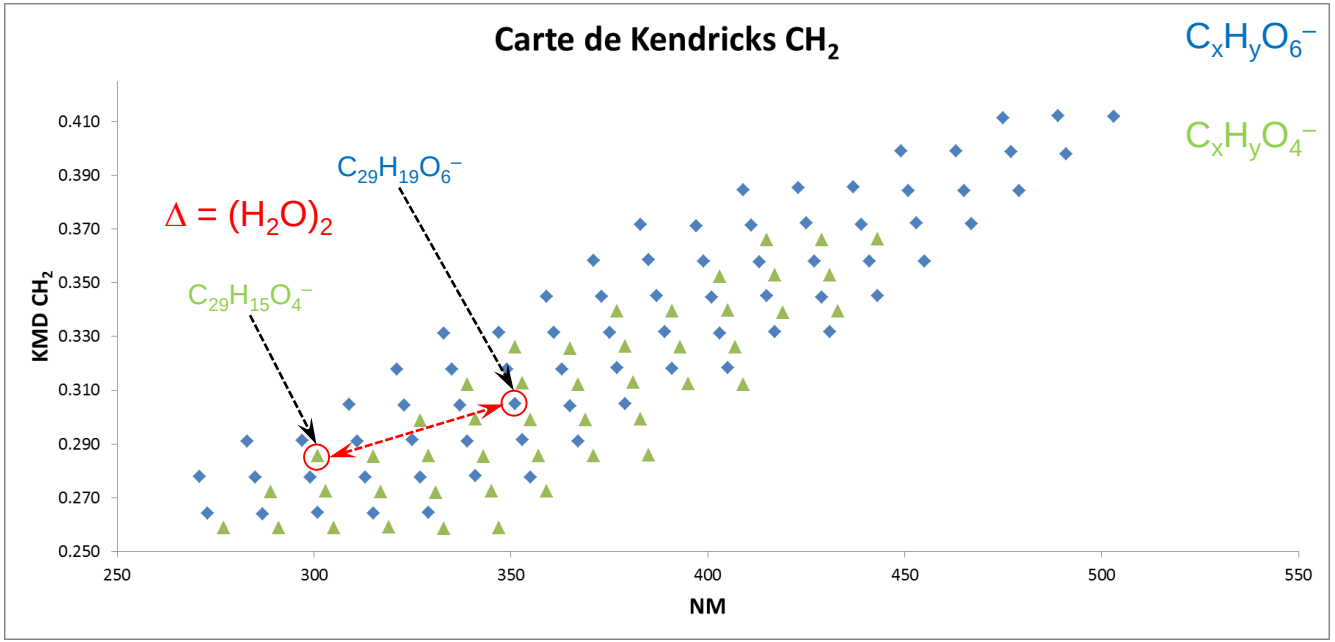
Marschall *et al. Acc. Chem. Res. 2004; 37: 53-59.*

Chlorinated contaminants



Taguchi *et al. JASMS 2011; 21: 1918-1921.*

Use of Kendrick mass for data assignment



Stepwise analysis – Principle of the main used search algorithms

From the Kendrick mass to the David mass

In complex a mixture, lot of its components are “correlated”: their chemical formulae only differ by one or a group of few atoms (on the mass spectrum: a given mass increment)

Principle

– increments which have to be searched

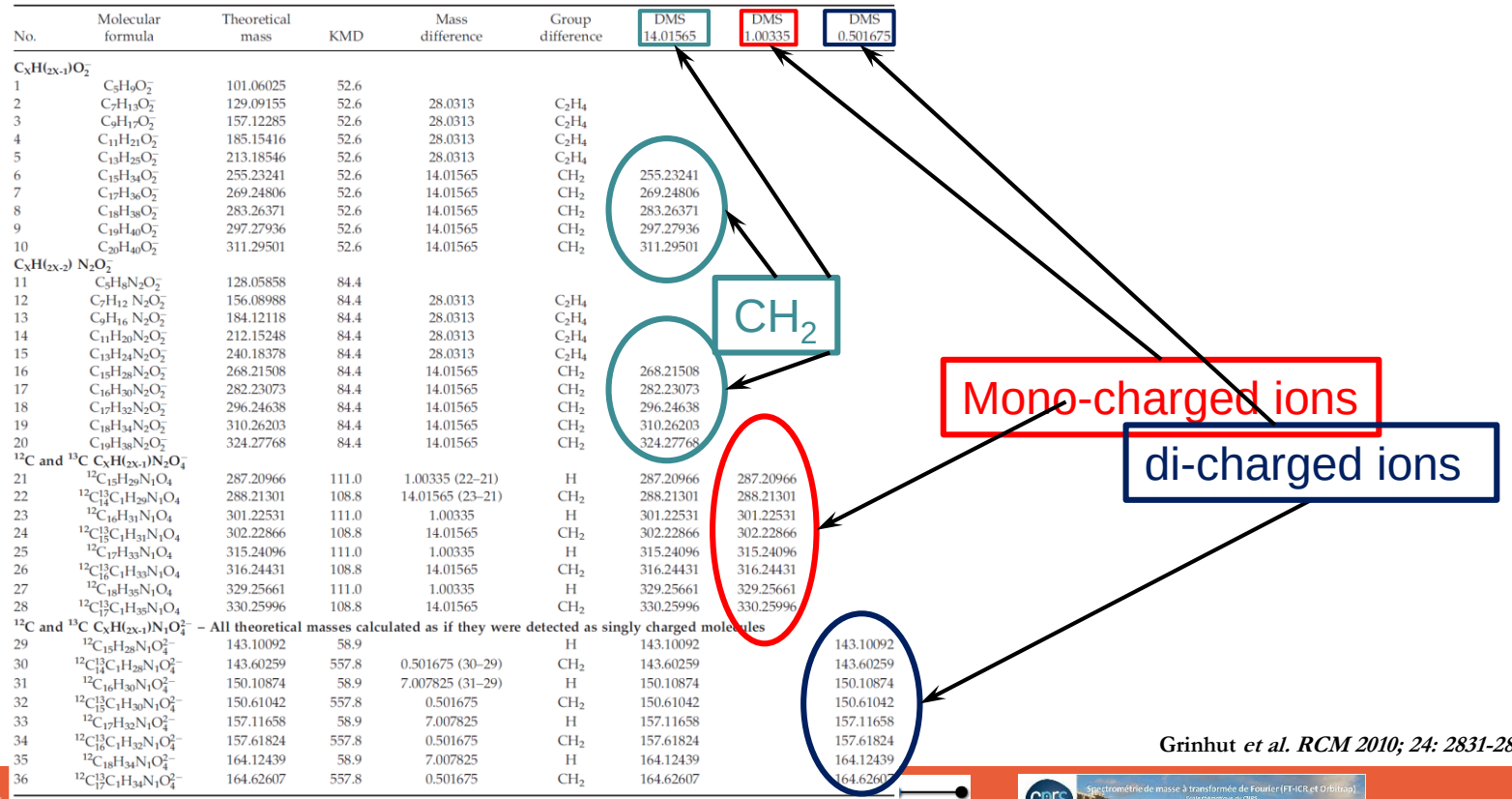
- 14.01465 ≡ CH_2
- 1.00335 ≡ ^{12}C – ^{13}C difference
- 1.00335/n ≡ ^{12}C – ^{13}C difference (multicharged ion)
- 30.01056 ≡ OCH_2
- …

– define the error, which has to be taken into account

Grinhut *et al. RCM 2010; 24: 2831-2837.*

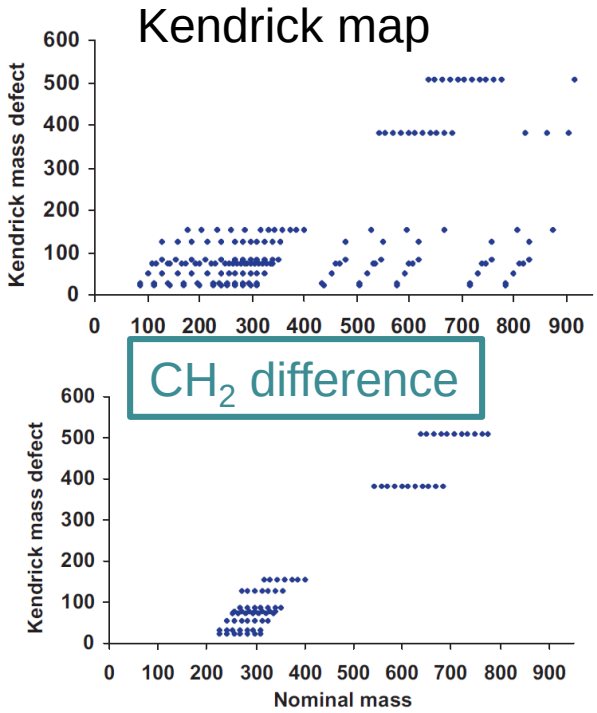
From the Kendrick mass to the David mass

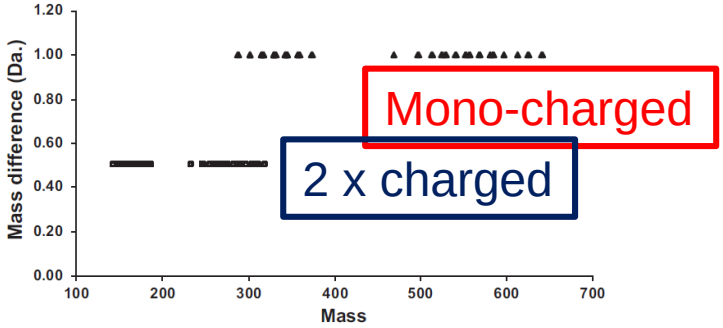
No.	Molecular formula	Theoretical mass	KMD	Mass difference	Group difference	DMS 14.01565	DMS 1.00335	DMS 0.501675
$C_XH_{(2X-1)}O_2^-$								
1	$C_5H_9O_2^-$	101.06025	52.6					
2	$C_7H_{13}O_2^-$	129.09155	52.6	28.0313	C_2H_4			
3	$C_9H_{17}O_2^-$	157.12285	52.6	28.0313	C_2H_4			
4	$C_{11}H_{21}O_2^-$	185.15416	52.6	28.0313	C_2H_4			
5	$C_{13}H_{25}O_2^-$	213.18546	52.6	28.0313	C_2H_4			
6	$C_{15}H_{34}O_2^-$	255.23241	52.6	14.01565	CH_2	255.23241		
7	$C_{17}H_{36}O_2^-$	269.24806	52.6	14.01565	CH_2	269.24806		
8	$C_{18}H_{38}O_2^-$	283.26371	52.6	14.01565	CH_2	283.26371		
9	$C_{19}H_{40}O_2^-$	297.27936	52.6	14.01565	CH_2	297.27936		
10	$C_{20}H_{40}O_2^-$	311.29501	52.6	14.01565	CH_2	311.29501		
$C_XH_{(2X-2)}\ N_2O_2^-$								
11	$C_5H_8N_2O_2^-$	128.05858	84.4					
12	$C_7H_{12}\ N_2O_2^-$	156.08988	84.4	28.0313	C_2H_4			
13	$C_9H_{16}\ N_2O_2^-$	184.12118	84.4	28.0313	C_2H_4			
14	$C_{11}H_{20}N_2O_2^-$	212.15248	84.4	28.0313	C_2H_4			
15	$C_{13}H_{24}N_2O_2^-$	240.18378	84.4	28.0313	C_2H_4			
16	$C_{15}H_{28}N_2O_2^-$	268.21508	84.4	14.01565	CH_2	268.21508		
17	$C_{16}H_{30}N_2O_2^-$	282.23073	84.4	14.01565	CH_2	282.23073		
18	$C_{17}H_{32}N_2O_2^-$	296.24638	84.4	14.01565	CH_2	296.24638		
19	$C_{18}H_{34}N_2O_2^-$	310.26203	84.4	14.01565	CH_2	310.26203		
20	$C_{19}H_{38}N_2O_2^-$	324.27768	84.4	14.01565	CH_2	324.27768		
^{12}C and $^{13}C\ C_XH_{(2X-1)}N_2O_4^-$								
21	$^{12}C_{15}H_{29}N_1O_4$	287.20966	111.0	1.00335 (22–21)	H	287.20966	287.20966	
22	$^{12}C_{14}^{13}C_1H_{29}N_1O_4$	288.21301	108.8	14.01565 (23–21)	CH_2	288.21301	288.21301	
23	$^{12}C_{16}H_{31}N_1O_4$	301.22531	111.0	1.00335	H	301.22531	301.22531	
24	$^{12}C_{15}^{13}C_1H_{31}N_1O_4$	302.22866	108.8	14.01565	CH_2	302.22866	302.22866	
25	$^{12}C_{17}H_{33}N_1O_4$	315.24096	111.0	1.00335	H	315.24096	315.24096	
26	$^{12}C_{16}^{13}C_1H_{33}N_1O_4$	316.24431	108.8	14.01565	CH_2	316.24431	316.24431	
27	$^{12}C_{18}H_{35}N_1O_4$	329.25661	111.0	1.00335	H	329.25661	329.25661	
28	$^{12}C_{17}^{13}C_1H_{35}N_1O_4$	330.25996	108.8	14.01565	CH_2	330.25996	330.25996	
^{12}C and $^{13}C\ C_XH_{(2X-1)}N_1O_4^{2-}$ – All theoretical masses calculated as if they were detected as singly charged molecules								
29	$^{12}C_{15}H_{28}N_1O_4^{2-}$	143.10092	58.9		H	143.10092		143.10092
30	$^{12}C_{14}^{13}C_1H_{28}N_1O_4^{2-}$	143.60259	557.8	0.501675 (30–29)	CH_2	143.60259		143.60259
31	$^{12}C_{16}H_{30}N_1O_4^{2-}$	150.10874	58.9	7.007825 (31–29)	H	150.10874		150.10874
32	$^{12}C_{15}^{13}C_1H_{30}N_1O_4^{2-}$	150.61042	557.8	0.501675	CH_2	150.61042		150.61042
33	$^{12}C_{17}H_{32}N_1O_4^{2-}$	157.11658	58.9	7.007825	H	157.11658		157.11658
34	$^{12}C_{16}^{13}C_1H_{32}N_1O_4^{2-}$	157.61824	557.8	0.501675	CH_2	157.61824		157.61824
35	$^{12}C_{18}H_{34}N_1O_4^{2-}$	164.12439	58.9	7.007825	H	164.12439		164.12439
36	$^{12}C_{17}^{13}C_1H_{34}N_1O_4^{2-}$	164.62607	557.8	0.501675	CH_2	164.62607		164.62607



Grinhut *et al. RCM 2010; 24: 2831-2837.*

From the Kendrick mass to the David mass





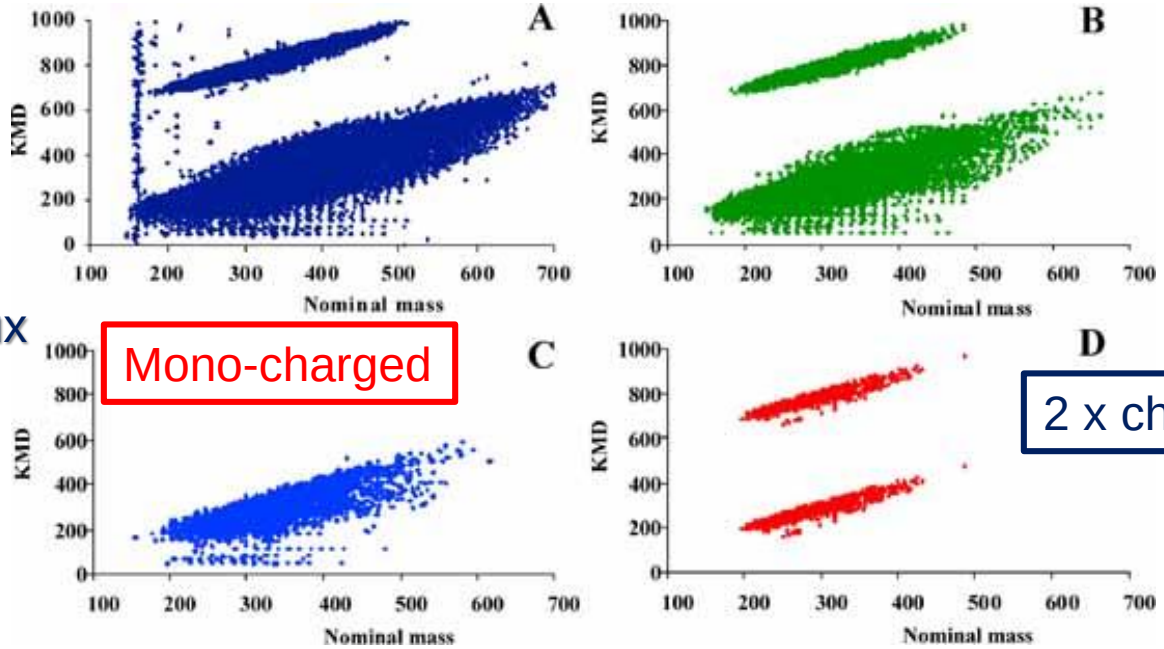
Grinhut *et al. RCM 2010; 24: 2831-2837.*

Application to the NOM analysis

15 420 signaux

Kendrick map

CH_2 increment



2 446 signaux

Mono-charged

1 065 signaux

2 x charged

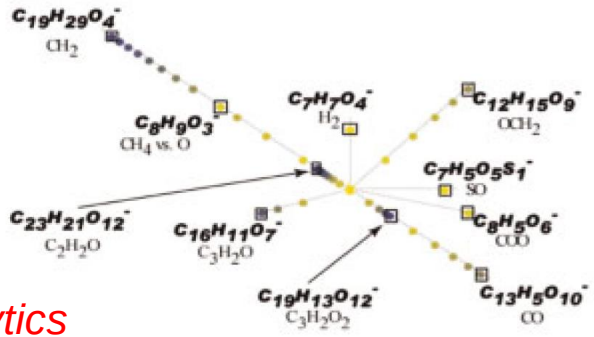
Grinhut *et al. RCM 2010; 24: 2831-2837.*

Application to the NOM analysis

Identification of only 10 repetitive units

- CH_2, OCH_2, CO, H_2, COO, H_2O, O_2, NH_3
- CH_4/O
- $O_2 - CH_4$

Use of a network based on the difference of mass for the assignment

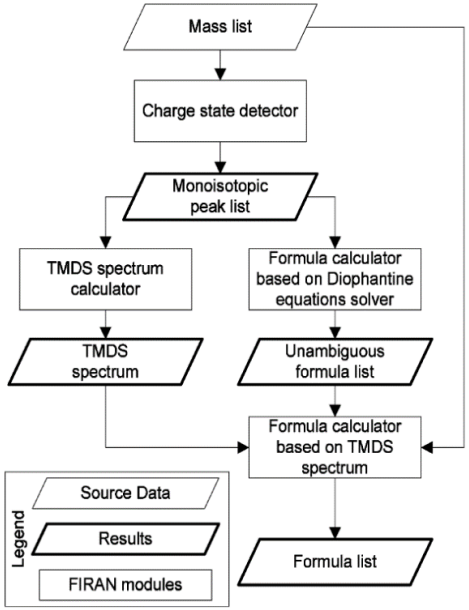


Logiciel Composer Sierra Analytics

Grinhut *et al. RCM 2010; 24: 2831-2837.*

The without *a priori* approach

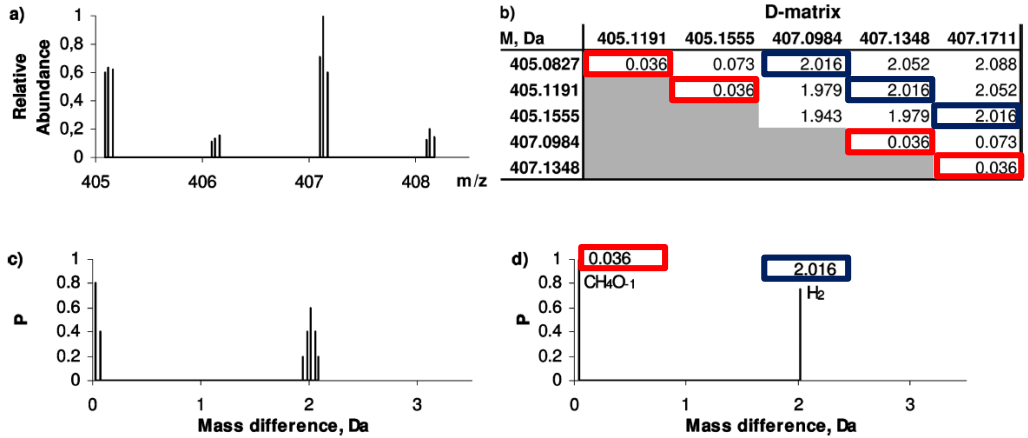
Same approach than David mass approach but without the prelimary definition of units



- Determination of the ion charge (m/z difference of 1.00335/n)
- Mono-isotopic peak list
- Generation of a matrice corresponding to the mass difference between each feature of the peak list
- Determination of the probability for each observed difference of mass
- TMDS spectrum (total mass difference statistics)
- Use of a cutoff for the low statistic

Kunenkov *et al. Anal Chem 2009; 81: 10106-10115.*

The without *a priori* approach

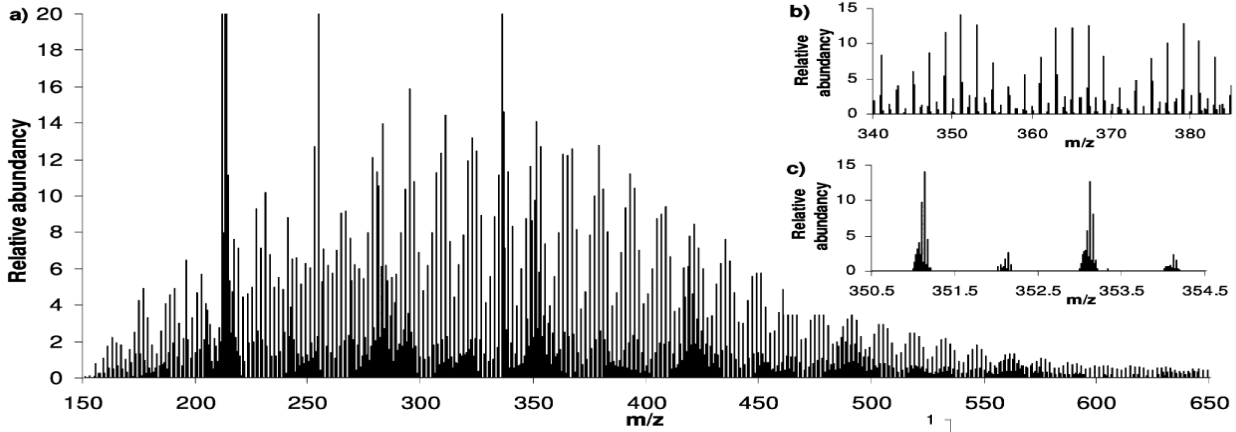


Stepwise assignment on the basis of the observed mass differences

- Increment of 2.016: addition of two hydrogen atoms
- Increment de 0.036: oxygen atom – CH_4 switching

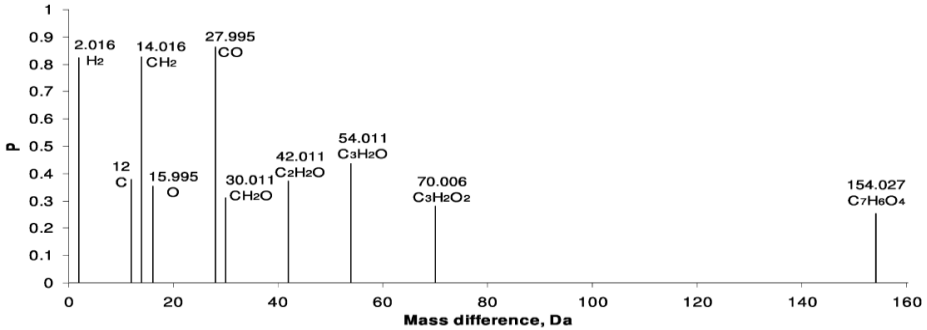
Kunenkov *et al. Anal Chem 2009; 81: 10106-10115.*

The without *a priori* approach



3 016 peaks

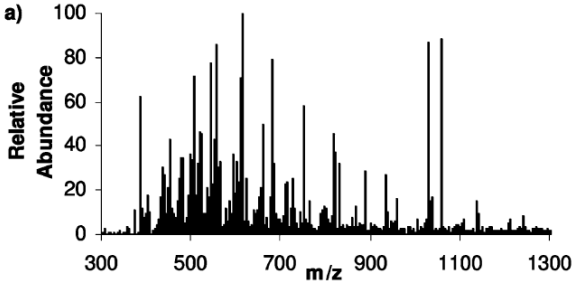
10 repeat units !!!

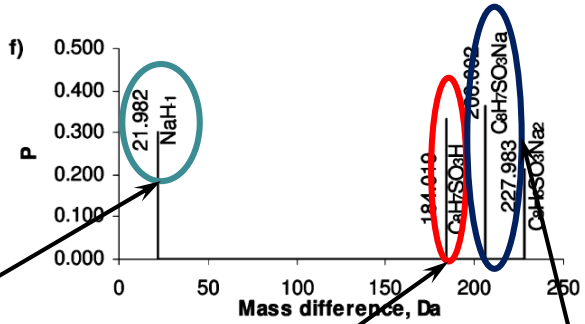


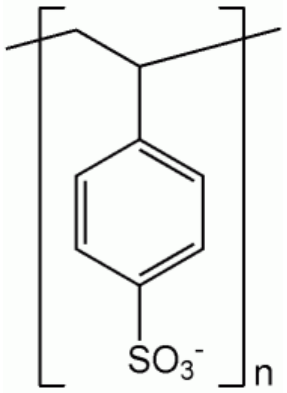
Kunenkov *et al. Anal Chem 2009; 81: 10106-10115.*

The without *a priori* approach

Sodium polystyren sulfonate







Protonated/ sodiated species

$(C_8H_7SO_3^-)_n$

Monomer styrene sulfonate

Monomer sodium styrene sulfonate

Kunenkov *et al. Anal Chem 2009; 81: 10106-10115.*

Use of second and third KMD orders

CH_2 first order mass defect

$$KM = measured\ mass \times \frac{14.00000}{14.01565} \qquad KMD(CH_2) = nominal\ mass - KM$$

- We will consider $C_{12+n}H_{26+2n-2z}$ (n = 0 – 10 et z = 1 – 5)
- It is preferable to take

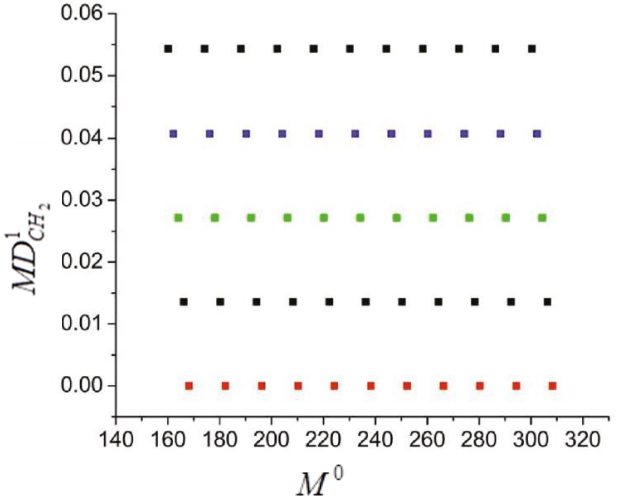
$$M^1_{CH_2}(ion) = \frac{arrondi(M^0_{CH_2}(CH_2))}{M^0_{CH_2}(CH_2)} \times M^0(ion)$$

  - For compouds with a positive KMD

$$MD^1_{CH_2} = M^1_{CH_2} - Plafond(M^1_{CH_2}, 1)$$

  - For compouds with a negative KMD

$$MD^1_{CH_2} = Plafond(M^1_{CH_2}, 1) - M^1_{CH_2}$$



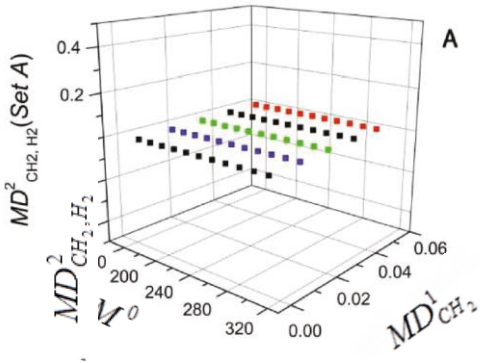
Roach *et al. Anal Chem 2011; 83: 4924-4929.*

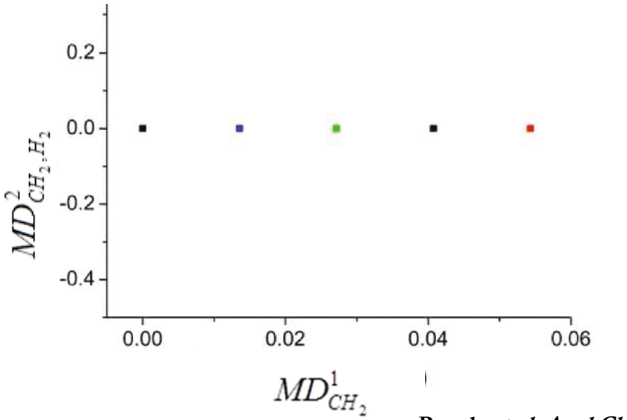
Use of second and third KMD orders

Second order H_2 / O mass defect calculation

$$M^{2}_{CH_2,H_2}(ion) = \frac{MD^{1}_{CH_2}(ion)}{MD^{1}_{CH_2}(H_2)} \qquad MD^{2}_{CH_2,H_2}(ion) = Plafond(M^{2}_{CH_2,H_2}(ion),1) - M^{2}_{CH_2,H_2}(ion)$$

$$M^{2}_{CH_2,O}(ion) = \frac{MD^{1}_{CH_2}(ion)}{MD^{1}_{CH_2}(O)} \qquad MD^{2}_{CH_2,O}(ion) = Plafond(M^{2}_{CH_2,O}(ion),1) - M^{2}_{CH_2,O}(ion)$$





Roach *et al. Anal Chem 2011; 83: 4924-4929.*

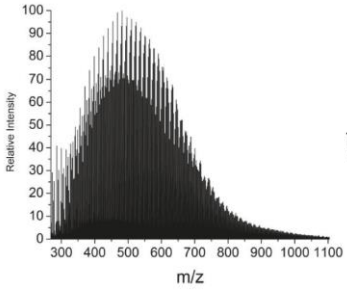
Use of second and third KMD orders

Third order mass defect O / H_2

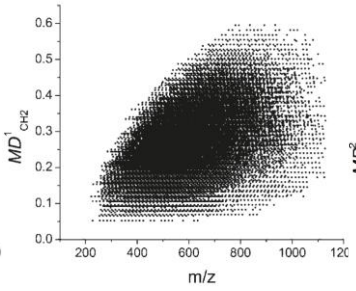
❶ $MD^3_{CH_2,H_2,O}(ion) = \mathrm{mod}[MD^2_{CH_2,H_2}(ion), MD^2_{CH_2,H_2}(O)]$

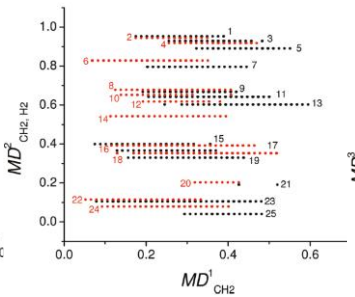
❷ $MD^3_{CH_2,O,H_2}(ion) = \mathrm{mod}[MD^2_{CH_2,O}(ion), MD^2_{CH_2,O}(H_2)]$

Be careful about the aliased points especially for ❶, mass defects are ranging from 0 to 1 according the used formulae, they have to be corrected by 1, 2, … to avoid aliasation

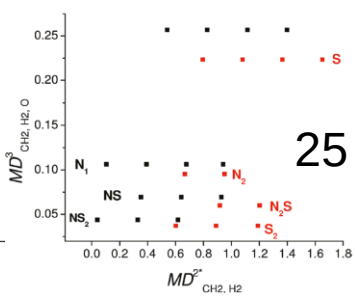


12 997 signals





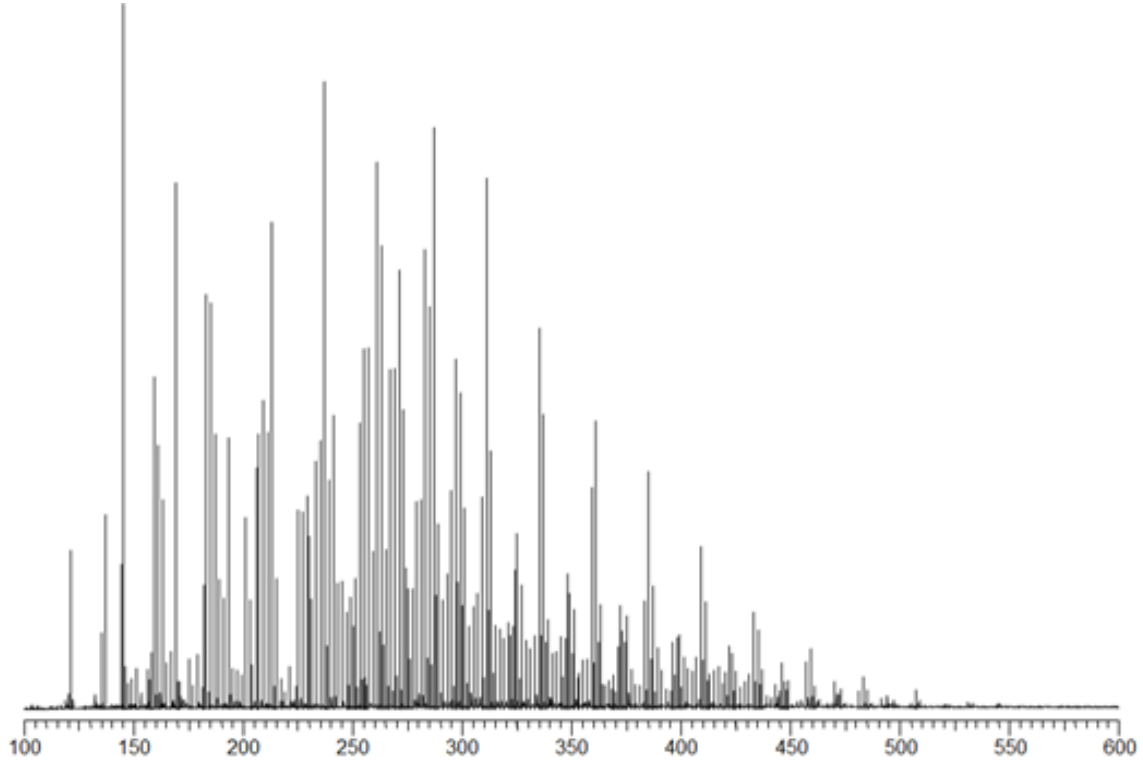
480 dots



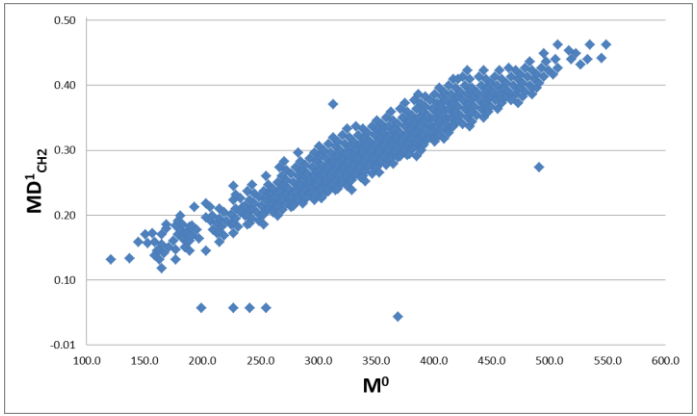
25 dots

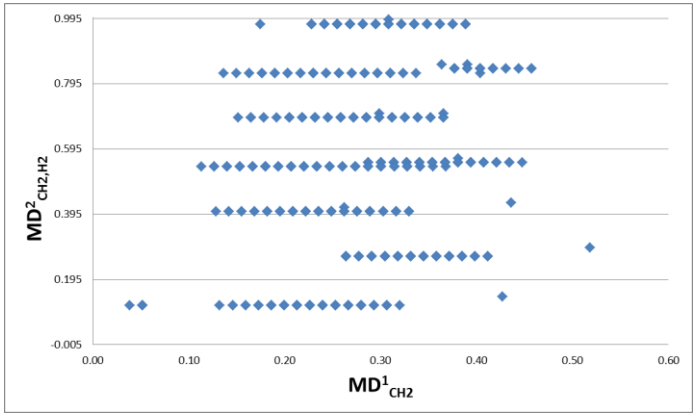
Roach *et al. Anal Chem 2011; 83: 4924-4929.*

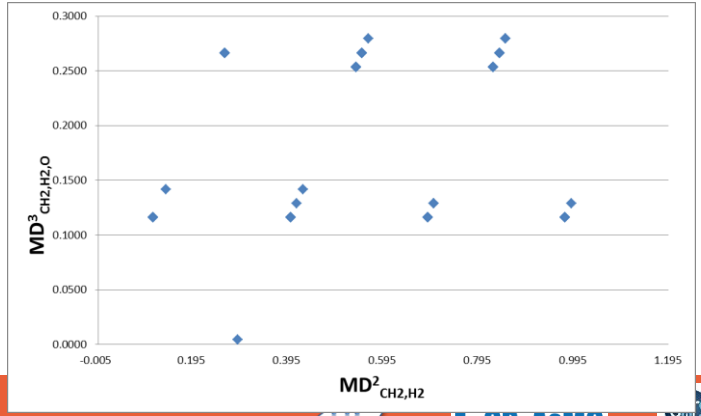
Representation of the data



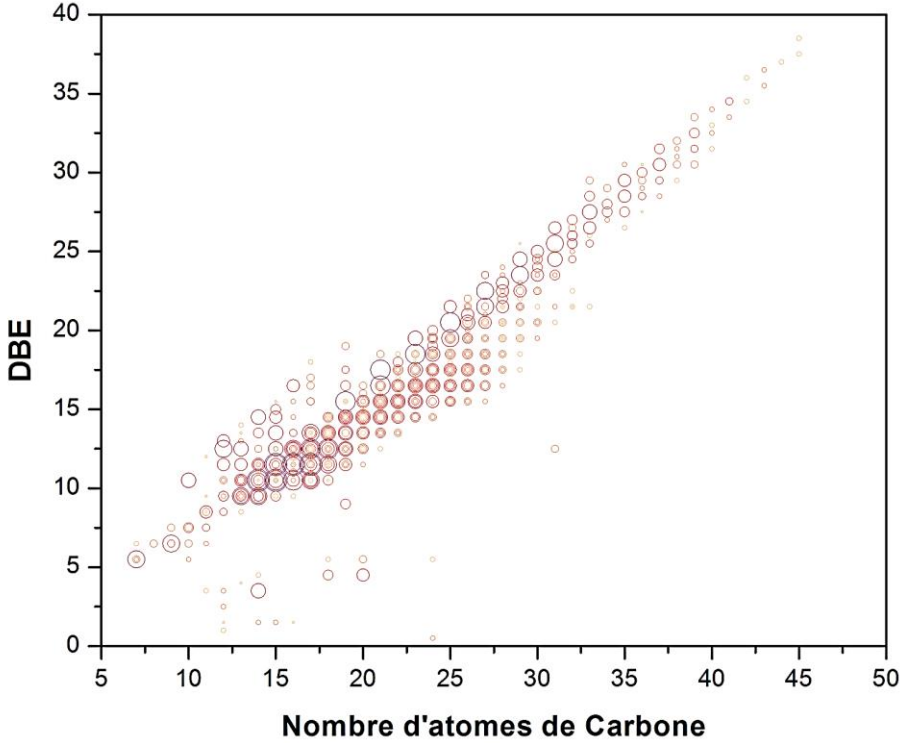
Representation of the data – Kendrick map



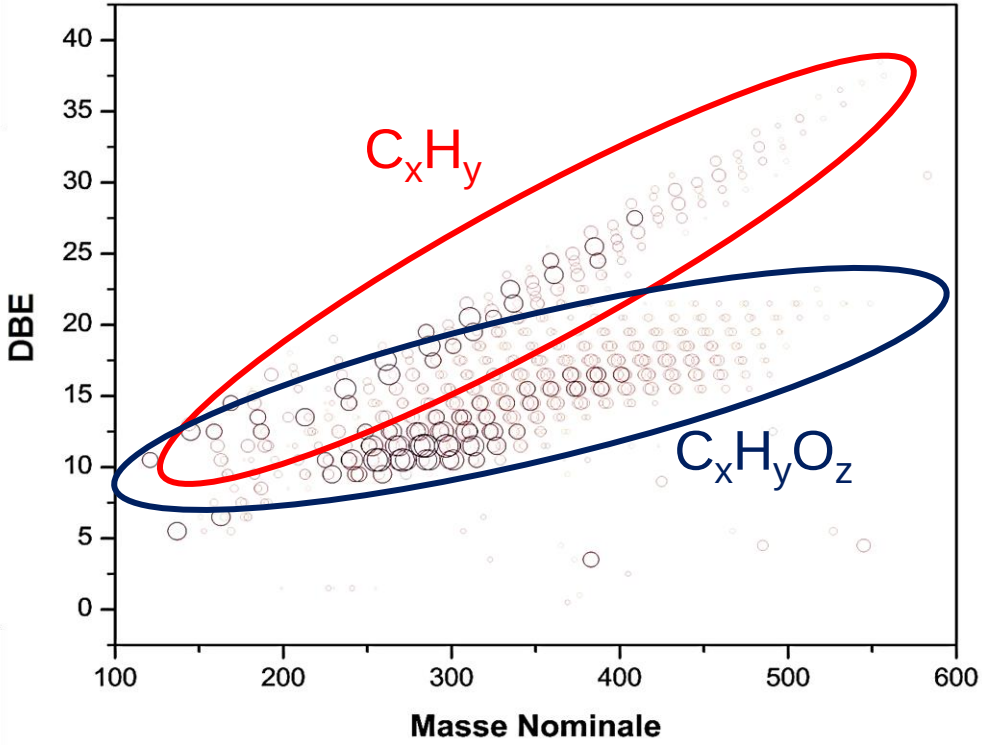




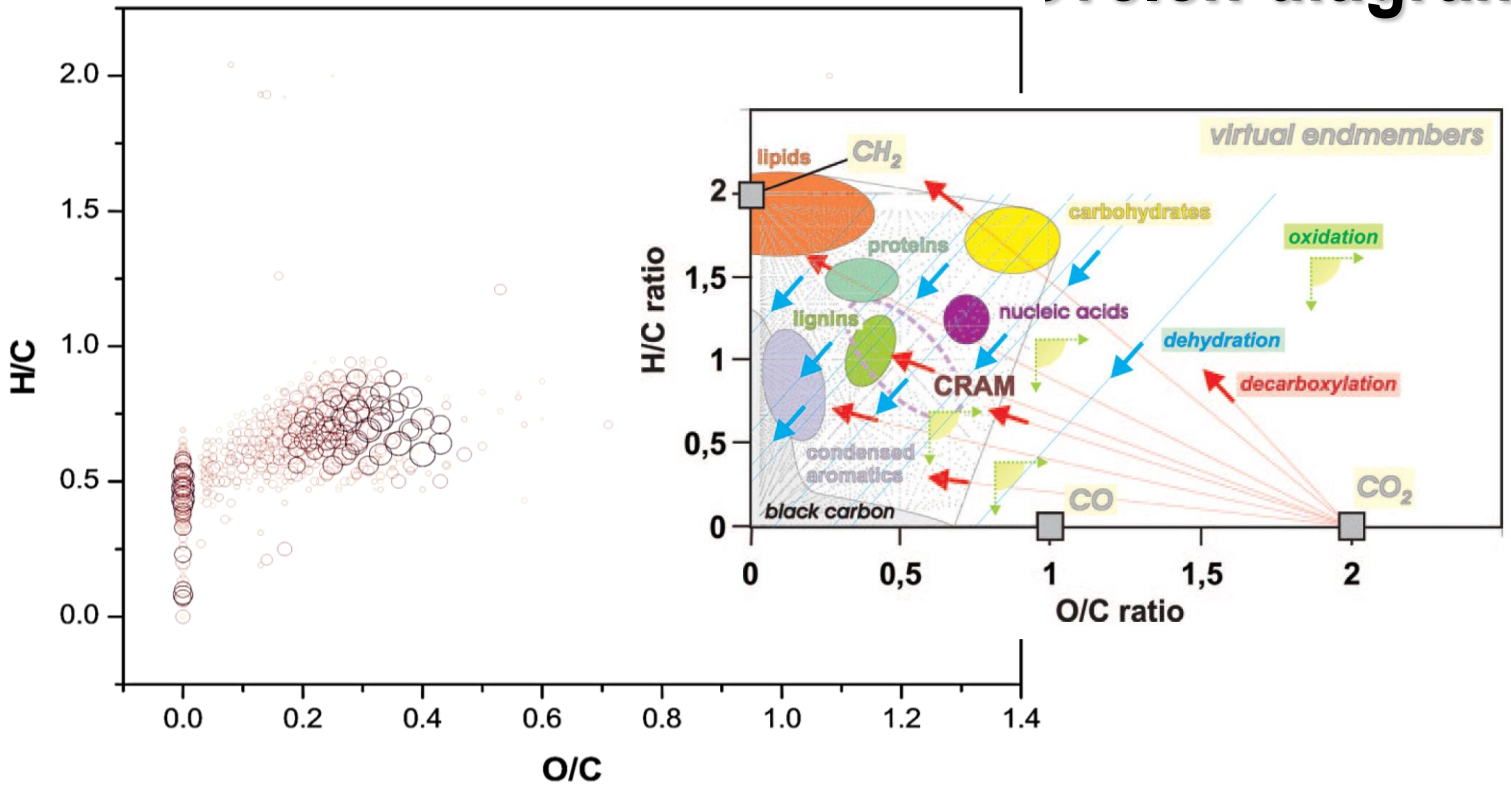
Representation of the data DBE *versus* # C



Representation of the data DBE versus m/z

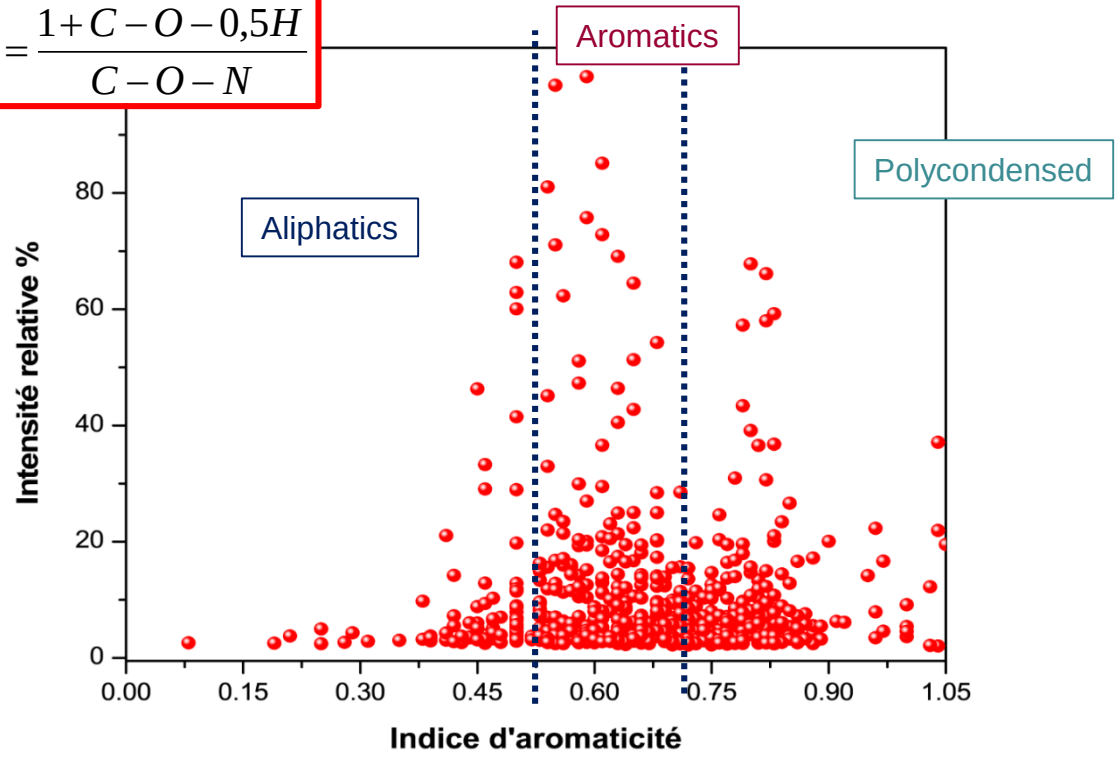


Representation of the data Van Krevelen diagram



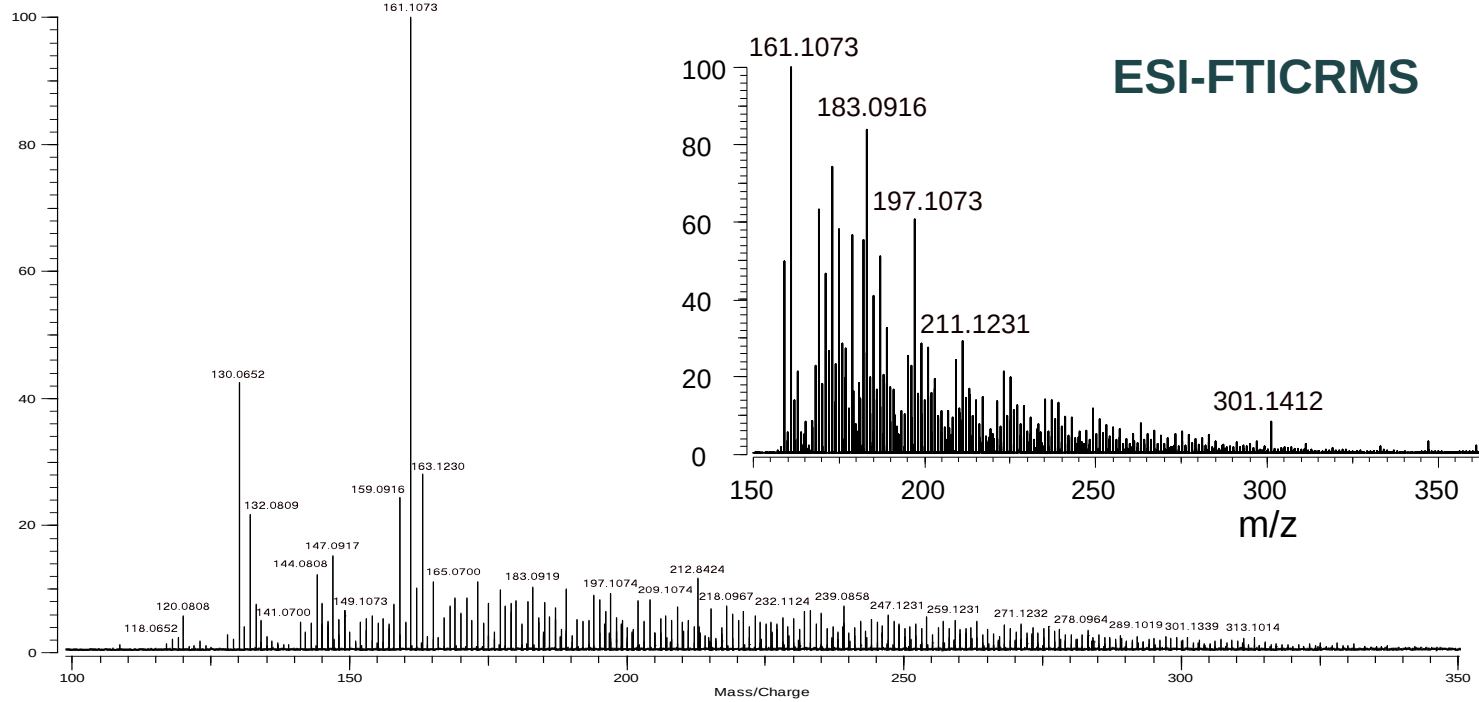
Representation of the data Aromaticity index

$$AI = \frac{1 + C - O - 0{,}5H}{C - O - N}$$

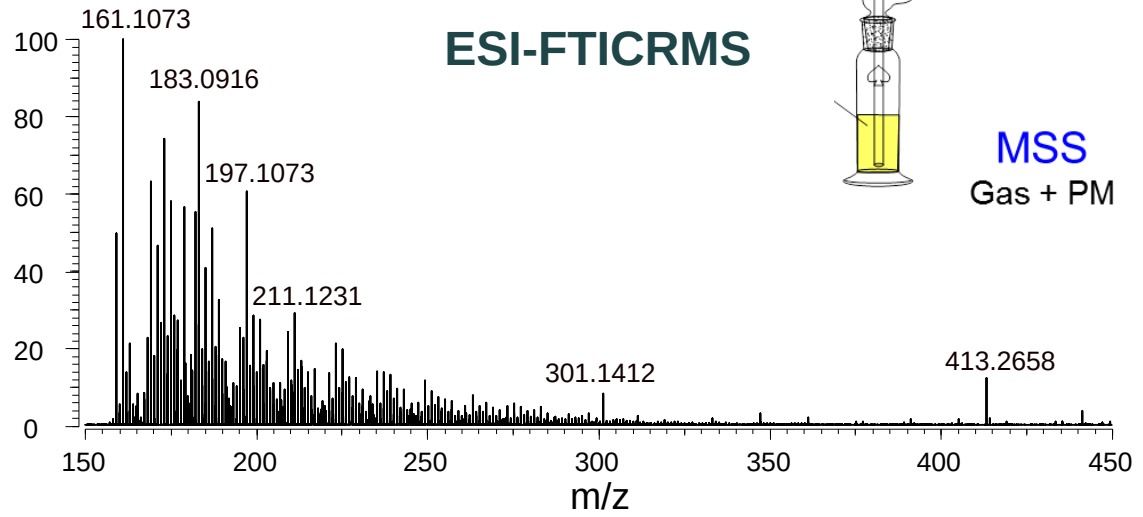


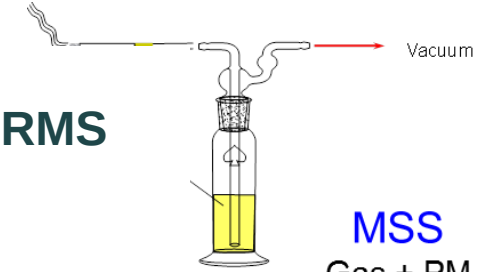
Study of cigarette smoke by ESI or LDI

LDI@355nm-FTICRMS

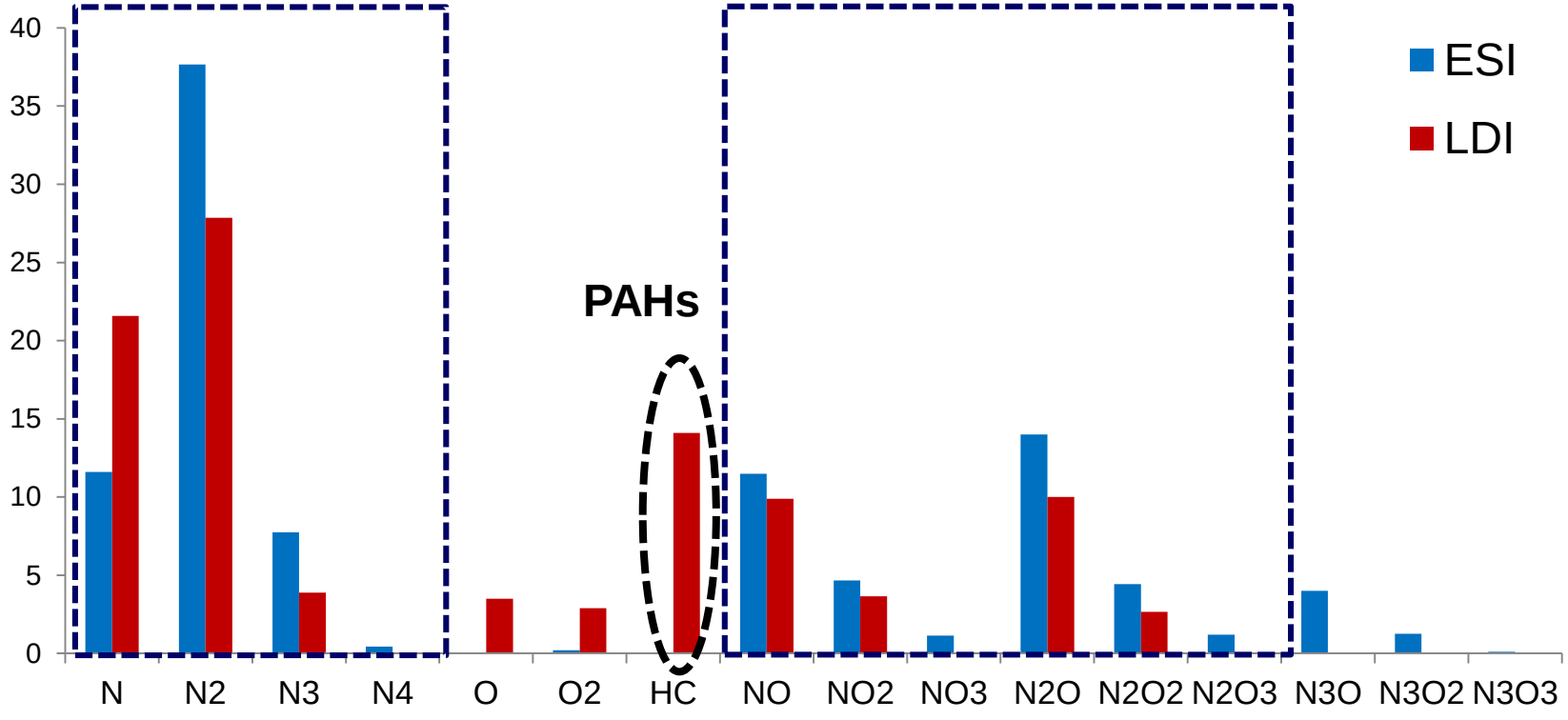


ESI-FTICRMS



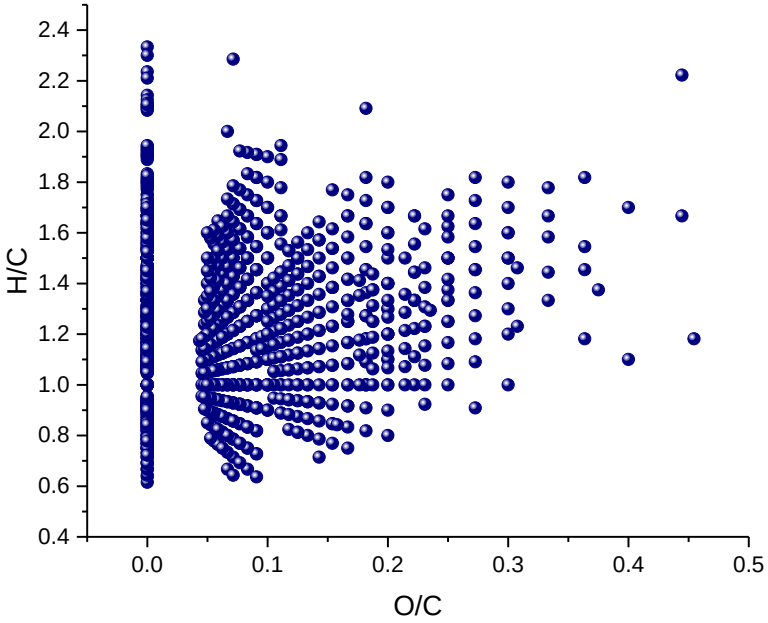


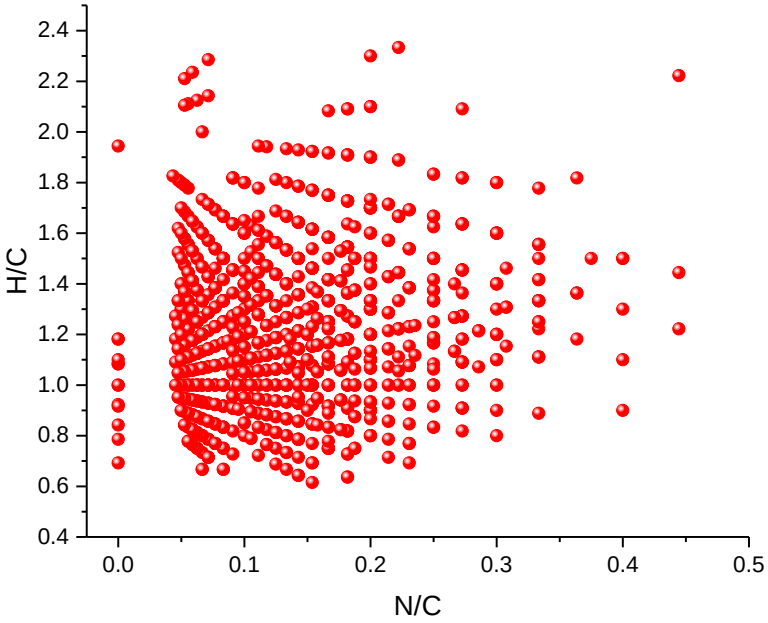
Complementarity of ESI and LDI



2D Van Krevelen Diagrams

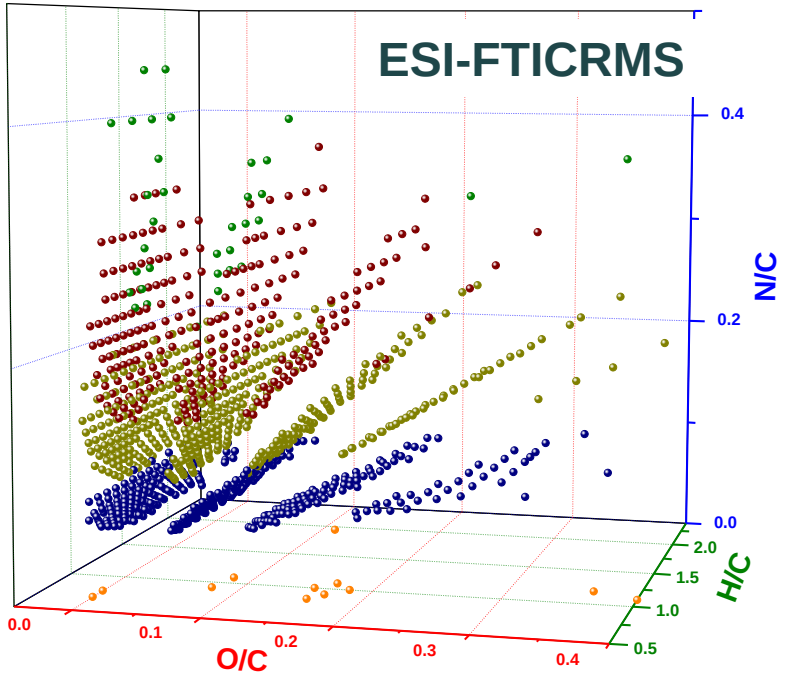
ESI-FTICRMS

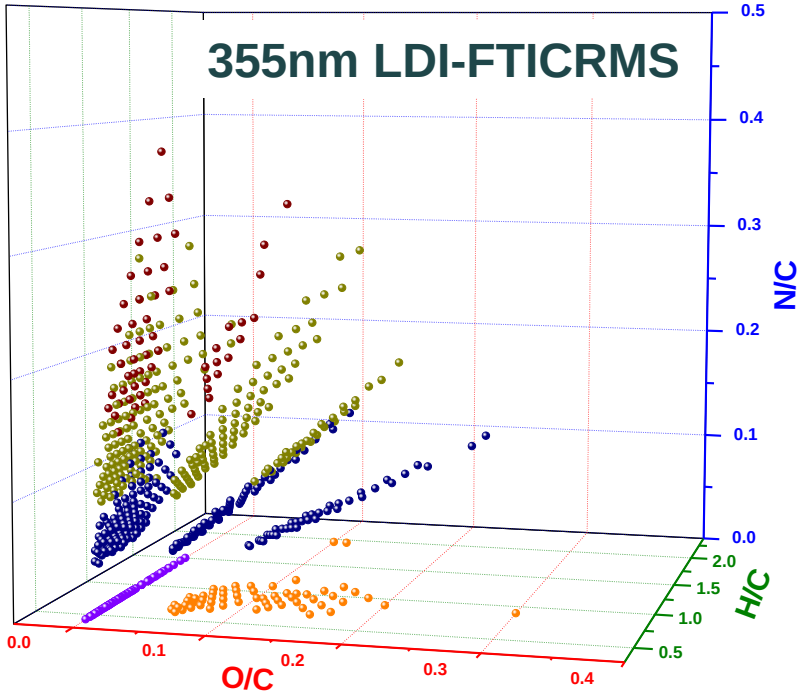


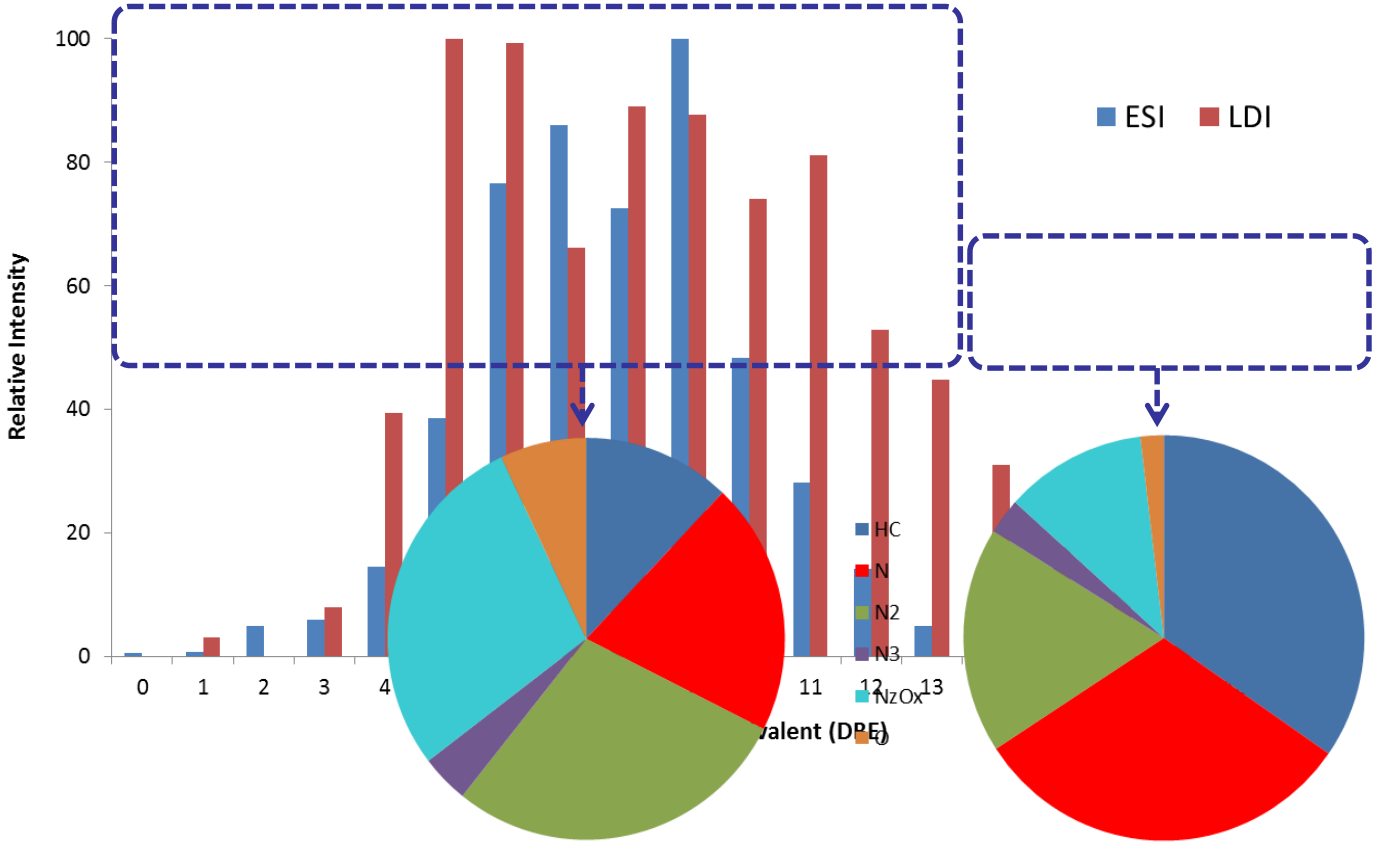


3D Van Krevelen Diagram

- $C_nH_mO_p^{+(\circ)}$
- $C_nH_mO_pN^{+(\circ)}$
- $C_nH_mO_pN_2^{+(\circ)}$
- $C_nH_mO_pN_3^{+(\circ)}$
- $C_nH_mO_pN_4^{+(\circ)}$






100
80
60
40
20
0
Relative Intensity
0
1
2
3
4
11
12
13
ESI
LDI
HC
N
N2
N3
NzOx
O

Proposition thèse MESR

Nouvelles approches pour l'étude de particules atmosphériques et de leur vieillissement par spectrométrie de masse ultra-haute résolution

Aubriet Frédéric – Sébastien Schramm

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