Universität Rostock Traditio et Innovatio | HelmholtzZentrum münchen Deutsches Forschungszentrum für Gesundheit und Umwelt

JOINT MASS SPECTROMETRY CENTRE

Lecture I:

Hands-on – direct infusion electrospray ionisation Fourier transform ion-cyclotron resonance mass spectrometry ESI FT-ICR MS

Dr. Christopher P. Rüger

Joint Mass Spectrometry Centre – University of Rostock and Helmholtz Zentrum München

1st EU_FT-ICR_MS network short course, Rostock 03/2018

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Outline

1) Revision theory ESI
2) Hardware
3) Experiments and data analysis
4) Summary

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Outline
Revision theory
Hardware
Experiments
Summary

Revision theory 1

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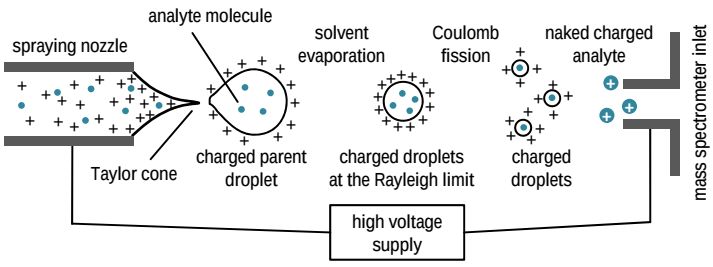
Outline
Revision theory
Hardware
Experiments
Summary

Basic function principle scheme



Doctorate Thesis, Christopher P. Rüger, University of Rostock, 2018

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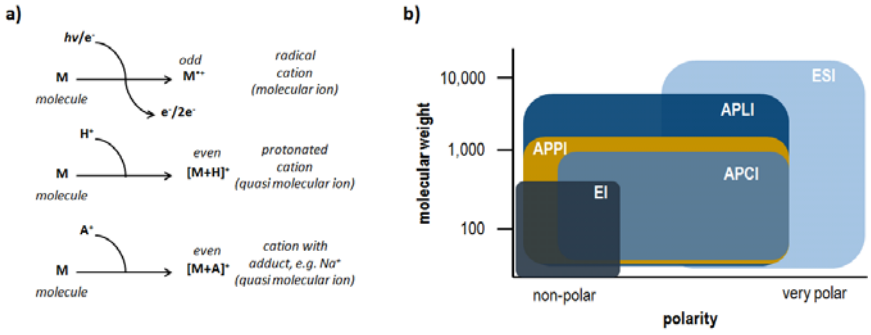
Revision theory

Outline | Revision theory | Hardware | Experiments | Summary

Basic function principle – preferred ionisation region



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Outline | Revision theory | Hardware | Experiments | Summary

Hardware 2

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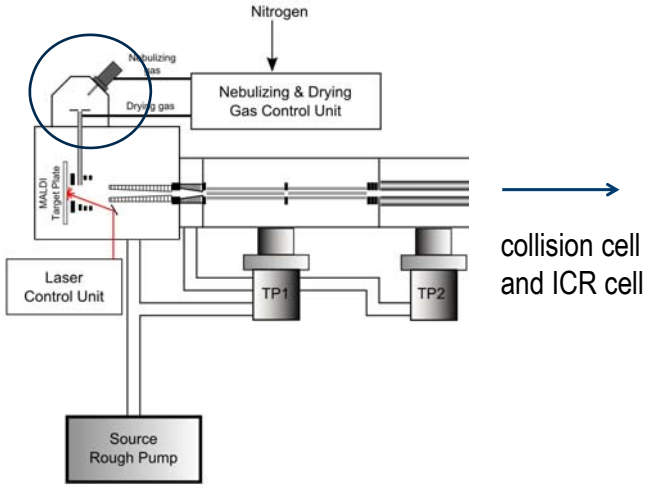
Hardware

Outline | Revision theory | Hardware | Experiments | Summary

Location at the instrument (off-axis) - Bruker



Bruker Daltonik, solarix FT-MS user manual, Revision 3 (March 2011), p. 40

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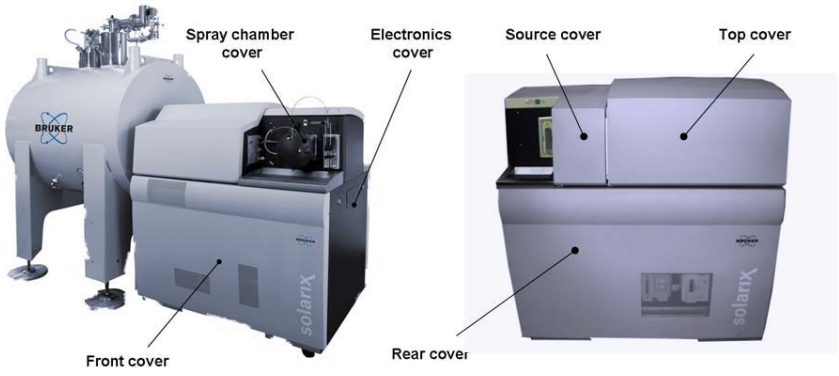
Hardware

Outline | Revision theory | Hardware | Experiments | Summary

Location at the instrument (off-axis) - Bruker



solariX Instrument Front View **solariX Instrument Rear View**

Bruker Daltonik, solarix FT-MS user manual, Revision 3 (March 2011), p. 43

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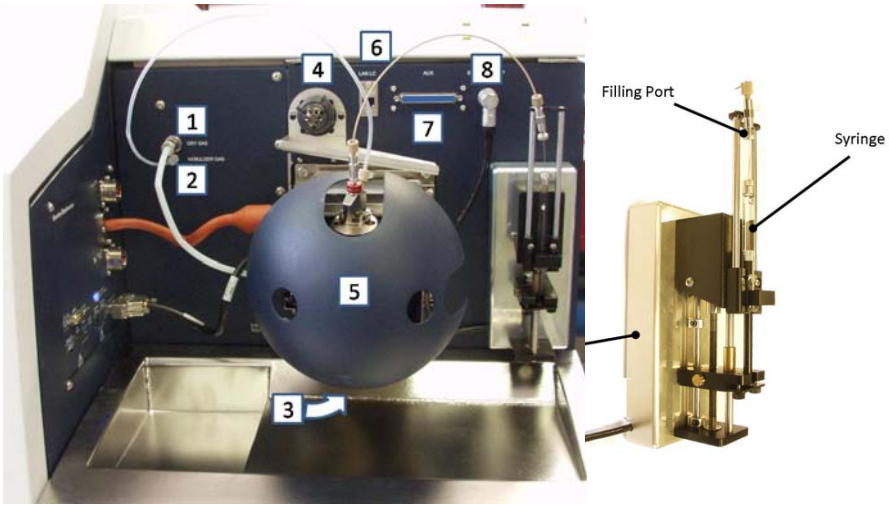
Hardware

Outline | Revision theory | Hardware | Experiments | Summary

Atmospheric pressure ionisation source - Bruker



Bruker Daltonik, solarix FT-MS user manual, Revision 3 (March 2011), p. 49

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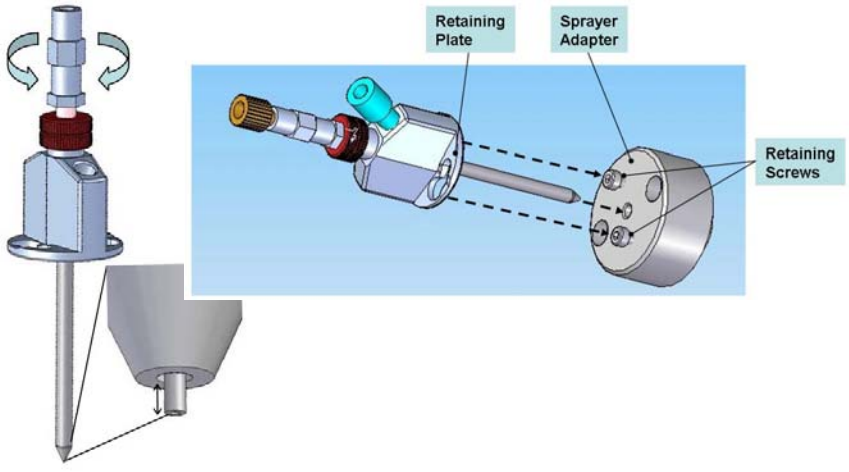
Hardware

Outline | Revision theory | Hardware | Experiments | Summary

Details electrospray sprayer unit



Bruker Daltonik, solarix FT-MS user manual, Revision 3 (March 2011), p. 130/132

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Outline
Revision theory
Hardware
Experiments
Summary

Experiments 3

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Outline
Revision theory
Hardware
Experiments
Summary

Experiments and data analysis

Experimental overview:

- Calibration standard: Arginine ($C_6H_{14}N_4O_2$, nominal mass: 174)
  - fine isotopic pattern → ^{13}C, ^{15}N, ^{2}H
  - varying resolving power
  - adaption of the ICR cell time-of-flight
  - declustering
  - acidification
  - negative mode
- Petroleomic samples: Marine gas oil (MGO) and light crude oil
  - general pattern and distribution
  - variation of spray-solvent (stability aspect – cell filling / space charge)

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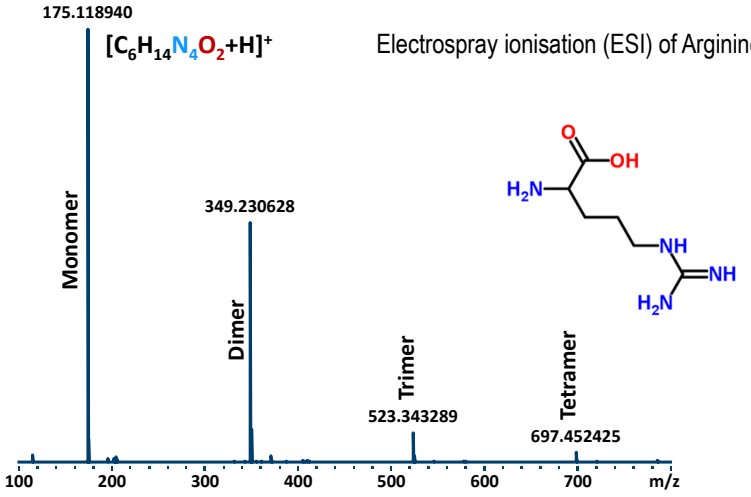
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Isotopic pattern and exact mass aspects



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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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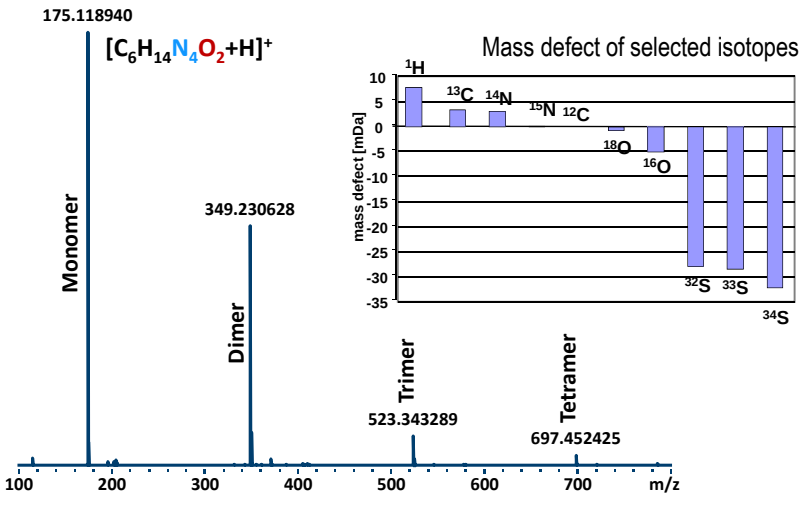

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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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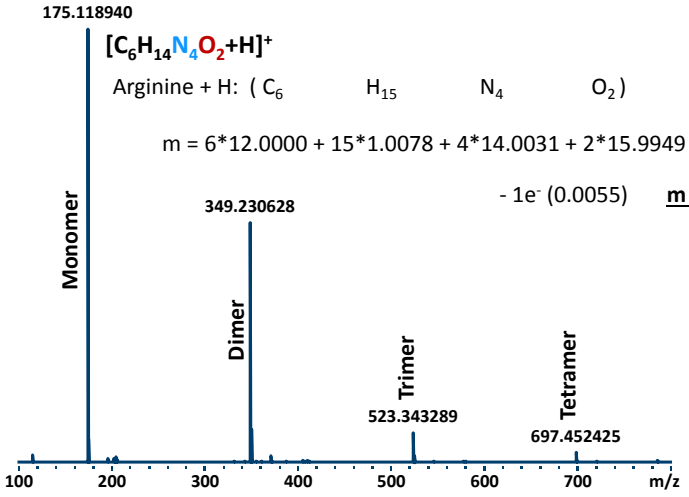

$[C_6H_{14}N_4O_2+H]^+$

Arginine + H: (C_6 H_{15} N_4 O_2)

m = 6*12.0000 + 15*1.0078 + 4*14.0031 + 2*15.9949 = **175.11950**

- $1e^-$ (0.0055) **m = 175.11895**

I. ppm mass accuracy

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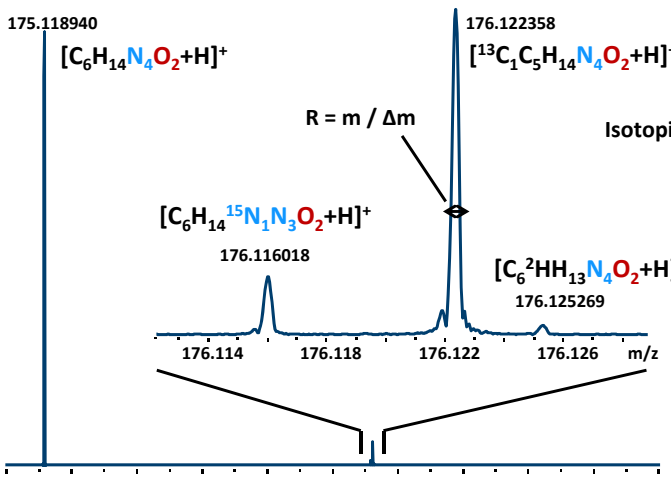
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Isotopic pattern and exact mass aspects



Isotopic fine structure

II. resolving power

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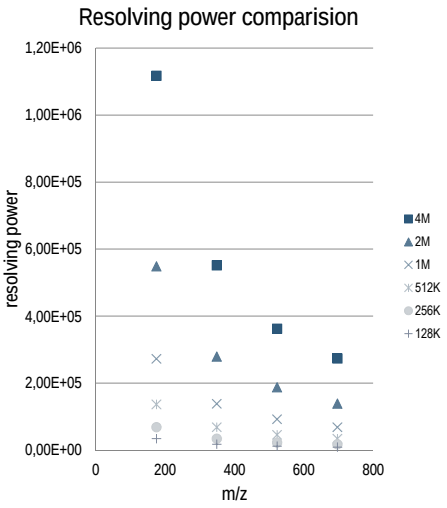
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Variation of the resolving power

Type	m/z	R	Setting
Monomer	175	1.12E+06	4M
Dimer	349	551371	4M
Trimer	523	362282	4M
Quatromer	697	273351	4M
Monomer	175	5.48E+05	2M
Dimer	349	278896	2M
Trimer	523	187585	2M
Quatromer	697	138955	2M
Monomer	175	2.73E+05	1M
Dimer	349	138271	1M
Trimer	523	92022	1M
Quatromer	697	67923	1M
Monomer	175	1.36E+05	512K
Dimer	349	68142	512K
Trimer	523	45514	512K
Quatromer	697	34143	512K
Monomer	175	6.86E+04	256K
Dimer	349	34399	256K
Trimer	523	22939	256K
Quatromer	697	17276	256K
Monomer	175	3.43E+04	128K
Dimer	349	17215	128K
Trimer	523	11498	128K
Quatromer	697	8621	128K



inverse proportional (1/X) behaviour for resolving power versus m/z

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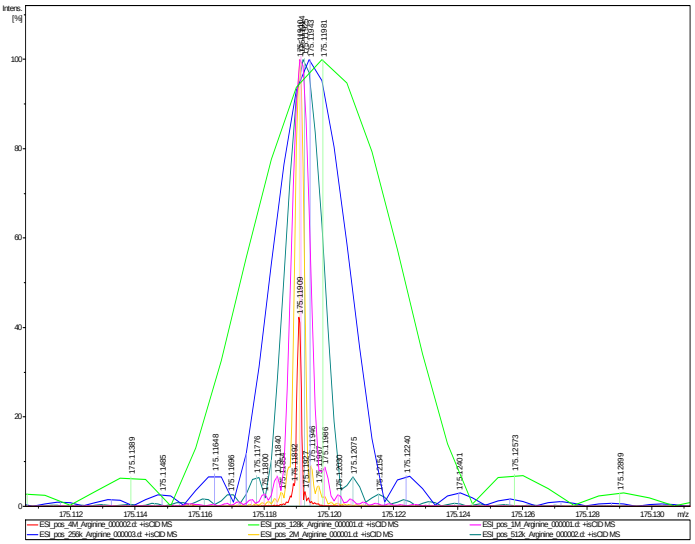
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Variation of the resolving power



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Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

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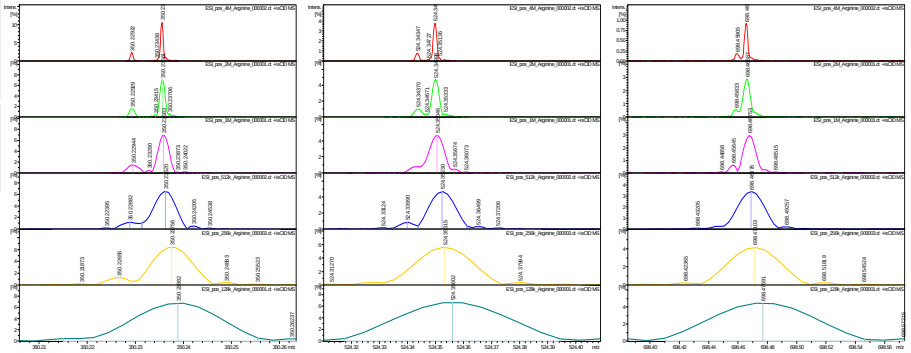

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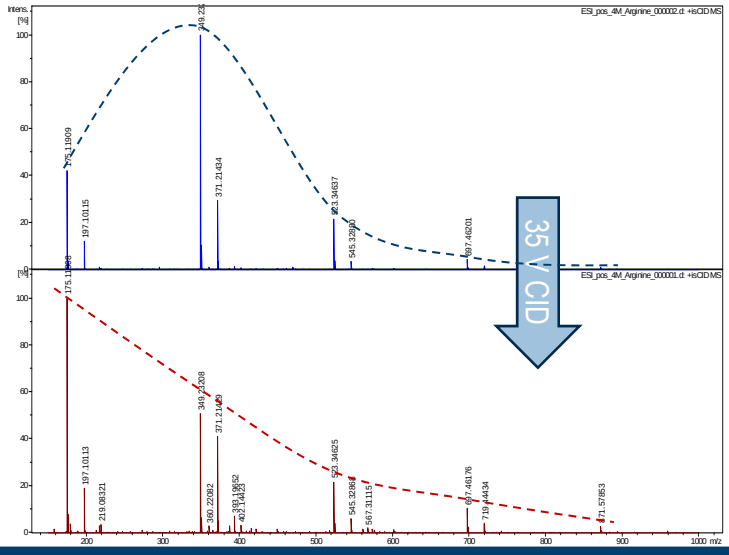
Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

Declustering – in-source collision induced dissociation (fragmentation)



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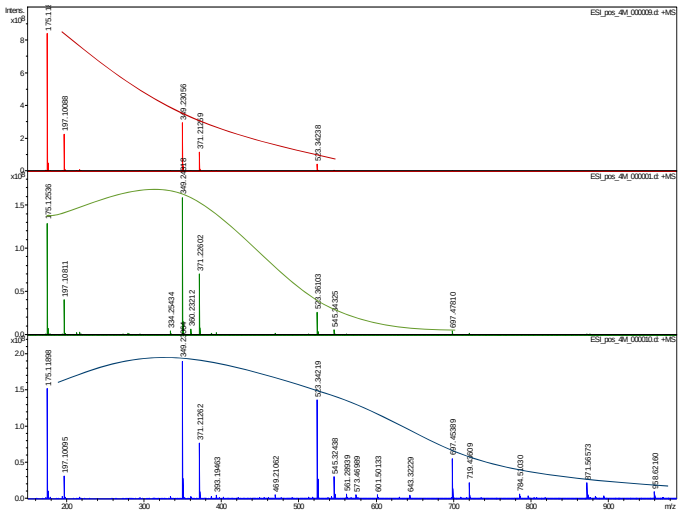
Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

Adaption of the ICR cell time-of-flight (TOF): 0.5, 0.7, 0.9 ms



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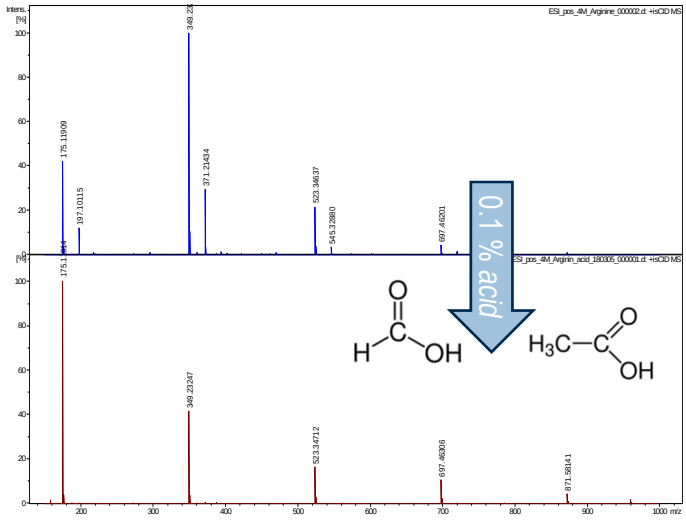
Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

Acidification – dopant for positive ion mode



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Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

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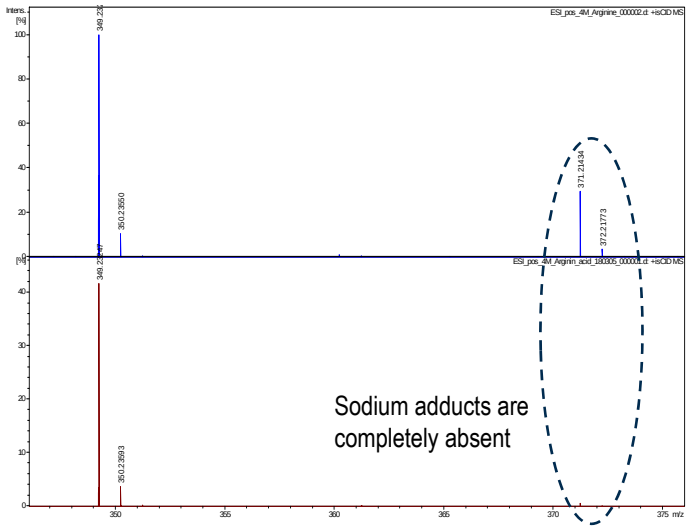

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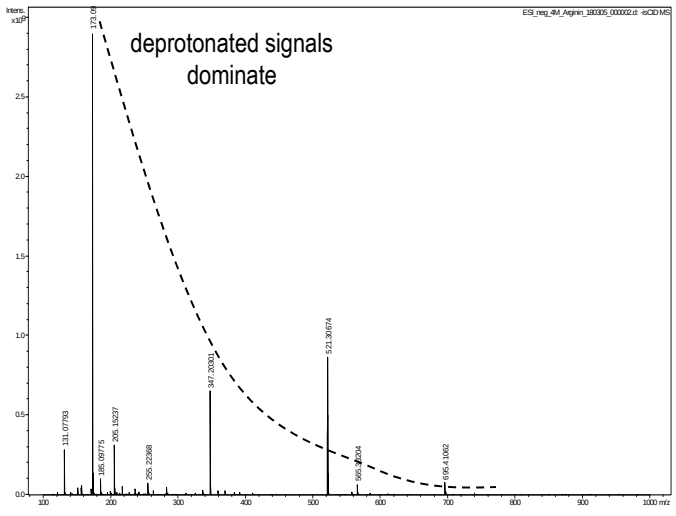
Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

A short look into negative mode electrospray ionisation



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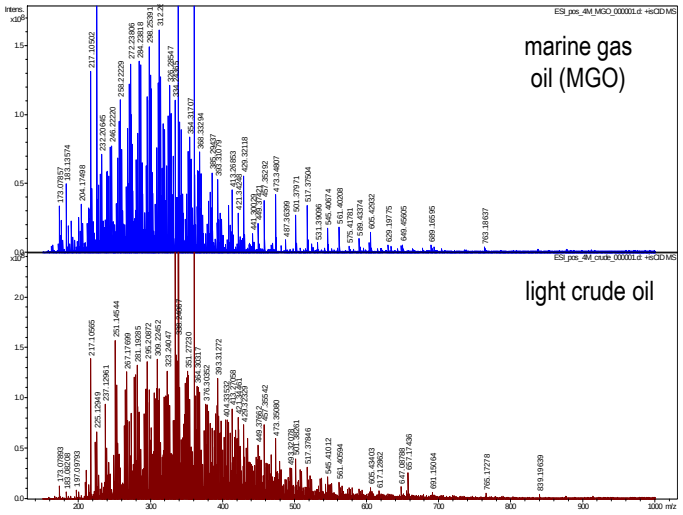
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Complex samples - Petroleomics



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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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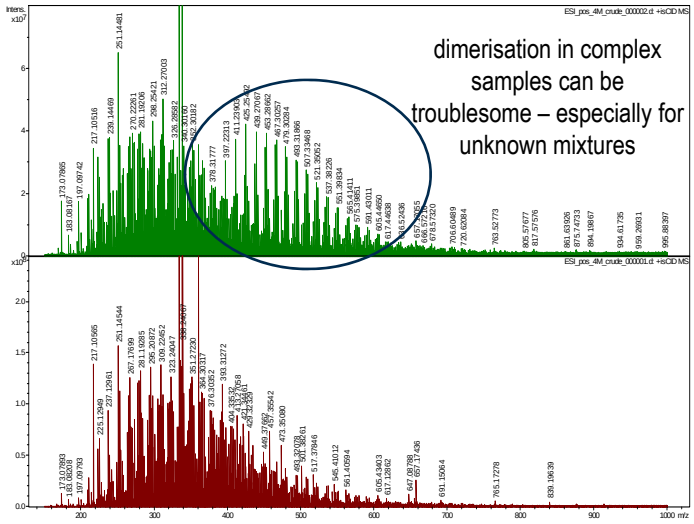

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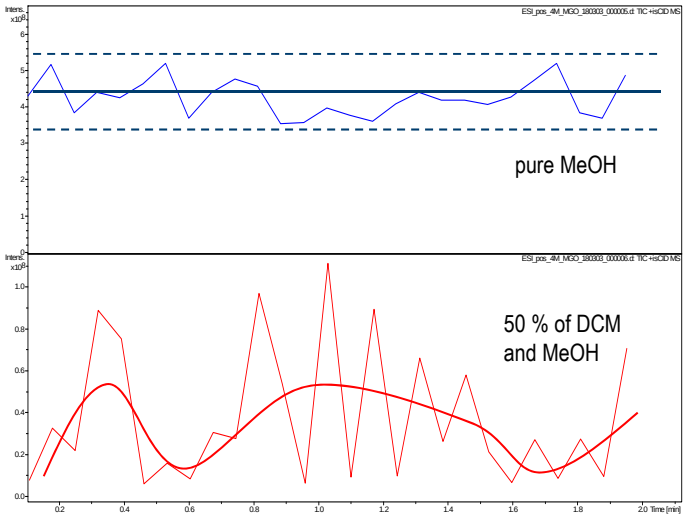
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Variation of the solvent – spray/signal stability aspects



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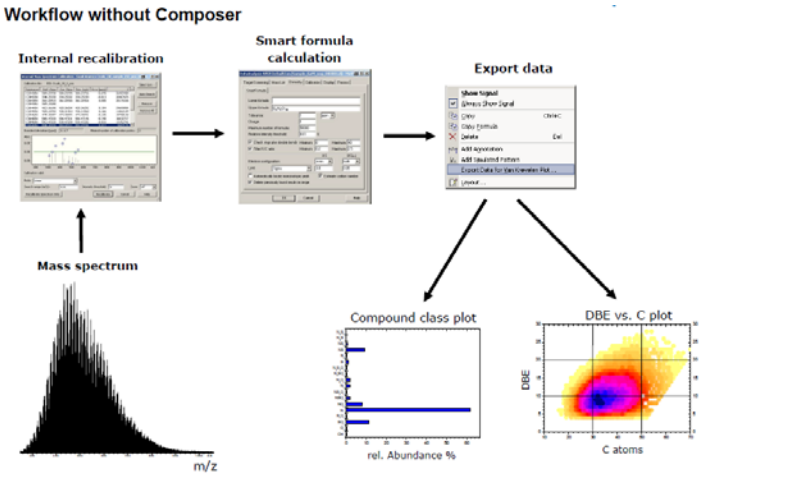
Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

Data analysis workflows – in brief



Complex mixture analysis by FT-ICR mass spectrometry, Matthias Witt, Bruker Daltonik

Experiments and data analysis

Data analysis workflows – in brief

Part of exported "VanKrevelen" csv-file from DataAnalysis

mSigma	Observed Intens	Observed m/z	calc. m/z	err mDa	err ppm	sum formula	C	H	N	O	S
108.35	8641884	300.1418	300.1417	-0.089	-0.295	C18 H22 N O S	18	22	1	1	1
16.3	1.62E+08	300.1747	300.1747	-0.001	-0.003	C22 H22 N	22	22	1	0	0
78.99	87776008	300.1781	300.178	-0.006	-0.019	C19 H26 N S	19	26	1	0	1
187.04	36897052	300.1906	300.1906	-0.012	-0.04	C20 H28 S	20	28	0	0	1
301.62	63234856	300.1992	300.1992	0.001	0.004	C16 H30 N O2 S	16	30	1	2	1
14.11	1.43E+08	300.2322	300.2322	-0.008	-0.027	C20 H30 N O	20	30	1	1	0
454.65	35209044	300.2355	300.2356	0.02	0.066	C17 H34 N O S	17	34	1	1	1
6.15	2.71E+09	300.2686	300.2686	-0.011	-0.037	C21 H34 N	21	34	1	0	0
138.26	11171612	301.1587	301.1587	-0.057	-0.19	C22 H21 O	22	21	0	1	0
274.12	13568545	301.1621	301.1621	-0.038	-0.127	C19 H25 O S	19	25	0	1	1
26.54	73958480	301.1951	301.1951	-0.002	-0.008	C23 H25	23	25	0	0	0
54.06	58521704	301.2162	301.2162	-0.004	-0.012	C20 H29 O2	20	29	0	2	0
19.98	1.09E+08	301.2526	301.2526	-0.015	-0.051	C21 H33 O	21	33	0	1	0
8.3	3.91E+08	301.256	301.256	0.009	0.03	C18 H37 O S	18	37	0	1	1
134.07	13690220	302.154	302.1539	-0.08	-0.265	C21 H20 N O	21	20	1	1	0
19.6	6.3E+08	302.1903	302.1903	-0.016	-0.06	C22 H24 N	22	24	1	0	0
180.24	2.02E+08	302.1937	302.1937	-0.007	-0.022	C19 H28 N S	19	28	1	0	1
458.67	26559926	302.2063	302.2063	-0.046	-0.152	C20 H30 S	20	30	0	0	1
144.49	2.13E+08	302.2148	302.2148	0.002	0.007	C16 H32 N O2 S	16	32	1	2	1
10.92	1.67E+08	302.2479	302.2478	-0.008	-0.028	C20 H32 N O	20	32	1	1	0
56.78	58798004	302.2512	302.2512	-0.004	-0.014	C17 H36 N O S	17	36	1	1	1
9.56	1.39E+09	302.2842	302.2842	0	-0.001	C21 H36 N	21	36	1	0	0
307.56	11270154	303.1735	303.1737	0.148	0.487	C14 H27 N2 O3 S	14	27	2	3	1
34.14	30199052	303.1744	303.1743	-0.022	-0.072	C22 H23 O	22	23	0	1	0
145.66	38518032	303.1777	303.1777	-0.01	-0.034	C19 H27 O S	19	27	0	1	1
271.89	38146860	303.1982	303.1982	-0.037	-0.123	C22 H25 N	22	25	1	0	0
23.48	1.43E+08	303.2107	303.2107	-0.006	-0.019	C23 H27	23	27	0	0	0
16.16	65120096	303.2319	303.2319	-0.017	-0.055	C20 H31 O2	20	31	0	2	0
17.82	1E+08	303.2683	303.2682	-0.009	-0.03	C21 H35 O	21	35	0	1	0

This table is imported in Excel for further analysis.

Excel table is provided for the calculation of van Krevelen plots and DBE vs. C plots

Complex mixture analysis by FT-ICR mass spectrometry, Matthias Witt, Bruker Daltonik

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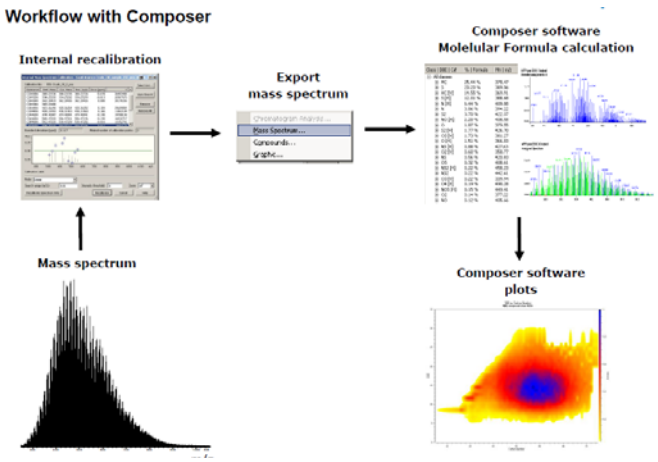
Experiments and data analysis

Outline
Revision theory
Hardware
Experiments
Summary

Comparison of ionisation techniques



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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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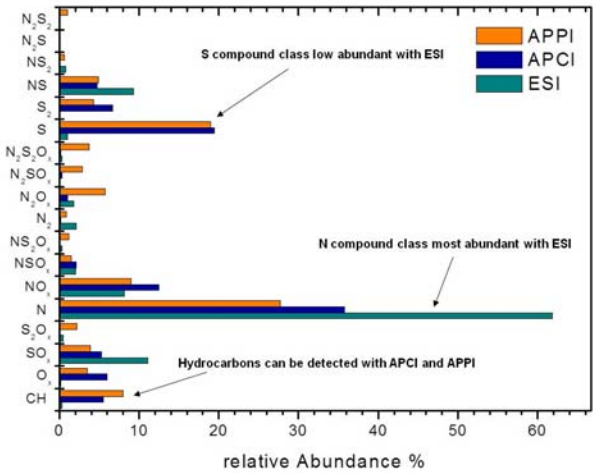

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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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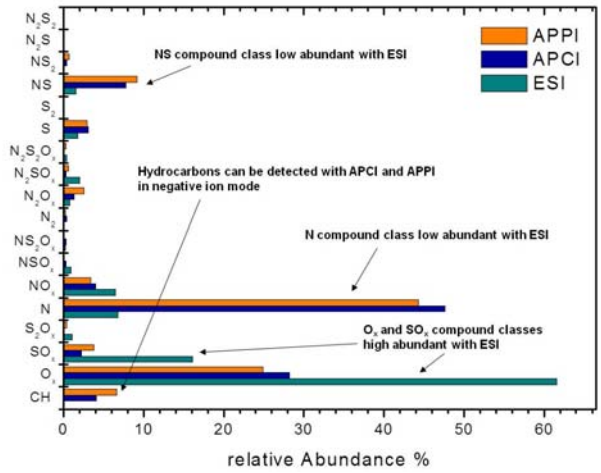

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Experiments and data analysis

Outline | Revision theory | Hardware | Experiments | Summary

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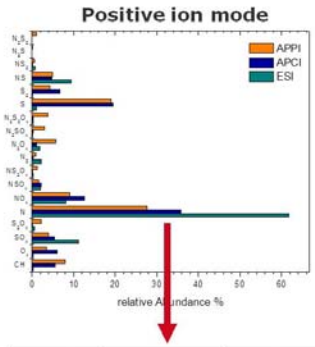

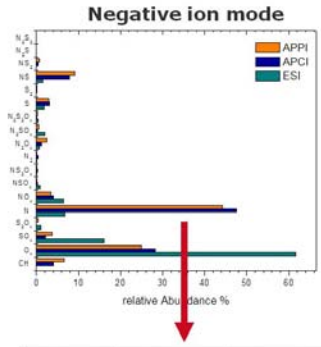

Ionization mode	carbon atom (average)	DBE (average)
ESI	35.3	11.0
APCI	33.1	11.3
APPI	40.1	13.4

Ionization mode	carbon atom (average)	DBE (average)
ESI	28.2	13.7
APCI	31.4	13.0
APPI	34.7	13.9

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Outline | Revision theory | Hardware | Experiments | Summary

Summary 4

HelmholtzZentrum münchen
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Summary

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Electrospray ionisation - Advantages and Drawbacks:

- ionizes very fragile molecules very gentle
- broad mass range of components can be covered
- easily interfaced with liquid chromatography and capillary electrophoresis

- very sensitive to salts (buffers)
- incompatible with some solvents
- not applicable to non(less)-polar compounds (see APCI/APPI)
- complex spectra can occur (adducts, multiple-charge stats etc.)