

## Actual Instrumentation

*December 2018*

See also <http://www.uni-bielefeld.de/chemie/analytik/ms> for additional information

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**General Remarks: For most instruments several experimental conditions are given. Choose the appropriate conditions used in your experiments and delete experimental conditions not matching your MS-data. In case of insecurities how to report MS-data refer to the head of the MS department.**

# 1. MALDI TOF Mass spectrometry on the Ultraflex

## experimental section:

Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) mixed on a steel target with 1  $\mu\text{L}$  of matrix solution (either 50 mg/mL 2,5-DHB in 50% ACN, 0,1% TFA or saturated DCTB in methanol). MALDI TOF mass spectra were recorded with a Ultraflex MALDI-TOF/TOF mass spectrometer (Bruker Daltonik, Bremen, Germany) operated in reflectron mode (For very large analytes, e.g. proteins: linear mode). Ionisation was achieved using a LTB nitrogen laser MNL 200 (337 nm beam wavelength, 50 Hz repetition rate). Maximum resolution achieved with this instrument is approx. 20,000.

### Calibration (choose relevant information):

The mass axis was externally calibrated with (PEG or fullerenes or red phosphorous<sup>1</sup>) as calibration standard on the same target.

or

The mass axis was internally calibrated with ... as internal calibration standard.

The spectra are recorded with FlexControl Software 3.0 (Bruker Daltonik, Bremen, Germany) by accumulation and averaging of (**enter number of shots, given on print out**) single laser shots. FlexAnalysis 3.4 (Bruker Daltonik, Bremen, Germany) was used for processing the spectra.

### specify (example):

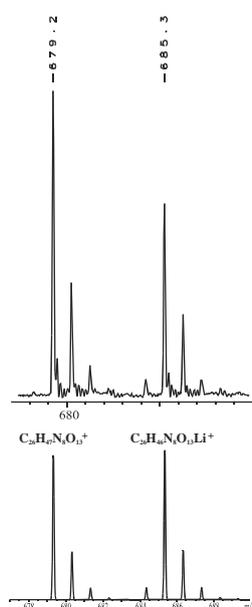
MS (MALDI TOF, positive ions, Matrix, Nr.of summed Spectra)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

MS (MALDI TOF, negative ions, Matrix, Nr.of summed Spectra)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_1 [\text{M}_1+\text{Cl}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**Comment : In MALDI, the most matrix compounds generate adduct ions. However, when DCTB is used as a matrix compound, radical cations are generated!  $\rightarrow m/z = \text{Mass}_1 [\text{M}_1]^{\bullet+}$**



*For soft ionisation techniques relative (!) intensities in the spectra should not be cited because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution.*

Example (or use example depicted in the Esquire 3000 section):

### abbreviations:

Mass<sub>x</sub>:  $m/z$  of the pseudomolecular ion; M<sub>x</sub>: number of the compound or it's formula (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)

Lit.: <sup>1</sup>Sladkova, K., Houska, J., Havel, J. Rapid Comm. Mass Spectrom. **2009**, *19*, 3114-3118

## 2. ESI mass spectrometry on the Esquire 3000

### experimental section:

Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) and introduced by static nano-ESI using *in-house* pulled glass emitters. Nitrogen served both as nebulizer gas and dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap and collision gas for MS<sup>n</sup> experiments. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard.

The spectra shown here are recorded with the Bruker Daltonik esquireNT 5.2 esquireControl software by the accumulation and averaging of several single spectra (as given in print outs). DataAnalysis™ software 3.4 was used for processing the spectra.

### specify (examples):

**MS** (ESI, positive ions)

$m/z = \text{Mass}_1 [M_1+H]^+, \text{Mass}_1 [M_1+Na]^+, \text{Mass}_1 [M_1+K]^+, \text{Mass}_2 [M_2+H]^+, \dots$

**MS** (ESI, negative ions)

$m/z = \text{Mass}_1 [M_1-H]^-, \text{Mass}_1 [M_1+Cl]^- , \text{Mass}_2 [M_2-H]^-, \dots$

**MS/MS** (ESI, P<sub>1</sub> ( $m/z$  XXX), positive ions)

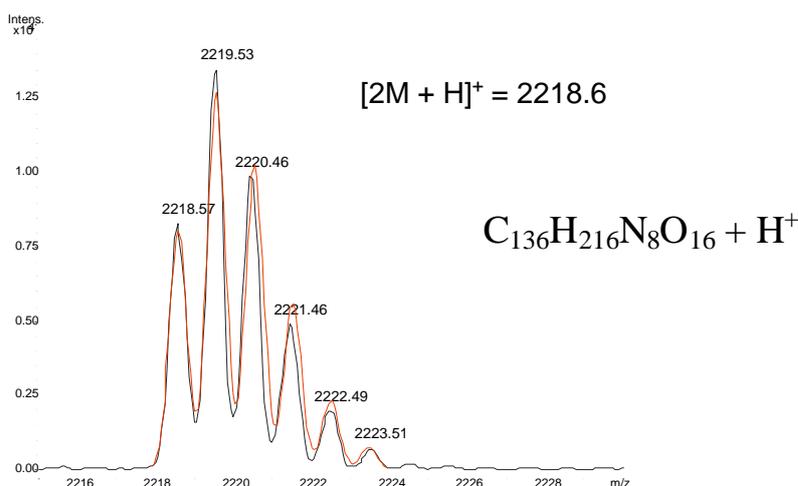
$m/z (\%) = P_1 [\text{precursor}]^+, D_1 (\text{int}) [\text{daughter 1}]^+, D_2 (\text{int}) [\text{daughter 2}]^+, \dots$

**MS<sup>3</sup>** (ESI, P<sub>1</sub> ( $m/z$  XXX) → P<sub>2</sub> ( $m/z$  YYY), positive ions)

$m/z (\%) = P_2 [\text{precursor}]^+, D_1 (\text{int}) [\text{daughter 1}]^+, D_2 (\text{int}) [\text{daughter 2}]^+, \dots$

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited (exception: MS<sup>n</sup> spectra) because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution.*

example:



### abbreviations:

Mass<sub>x</sub>:  $m/z$  of the pseudomolecular ion

M<sub>x</sub>: number of the compound or it's formula (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)

P<sub>x</sub>:  $m/z$  of the precursor ion

D<sub>x</sub>:  $m/z$  of the daughter ion

### 3. Accurate Mass ESI mass spectrometry on the Agilent 6220

#### experimental section:

ESI accurate mass measurements are acquired using an Agilent 6220 time-of-flight mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) in extended dynamic range mode equipped with a Dual-ESI source, operating with a spray voltage of 2.5 kV. Nitrogen served both as nebulizer gas and dry gas. Nitrogen was generated by a nitrogen generator NGM 11. Samples were dissolved in acetonitrile and introduced with a 1200 HPLC system consisting of an autosampler, degasser, binary pump, column oven and diode array detector (Agilent Technologies, Santa Clara, CA, USA) using a C18 Hypersil Gold column (length: 50 mm, diameter: 2.1 mm, particle size: 1.9  $\mu\text{m}$ ) with a short gradient (in 4 min from 0% B to 98% B, back to 0% B in 0.2 min, total run time 7.5 min) at a flow rate of 250  $\mu\text{L}/\text{min}$  and column oven temperature of 40°C. HPLC solvent A consists of 94.9% water, 5% acetonitrile and 0.1% formic acid, solvent B of 5% water, 94.9% acetonitrile and 0.1% formic acid.

The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard.

The mass spectra shown here are recorded in both profile and centroid mode with the MassHunter Workstation Acquisition B.04.00 software (Agilent Technologies, Santa Clara, CA, USA). MassHunter Qualitative Analysis B.07.00 software (Agilent Technologies, Santa Clara, CA, USA) was used for processing and averaging of several single spectra (details given in print outs).

#### specify (examples):

**MS** (ESI, positive ions)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

**MS** (ESI, negative ions)

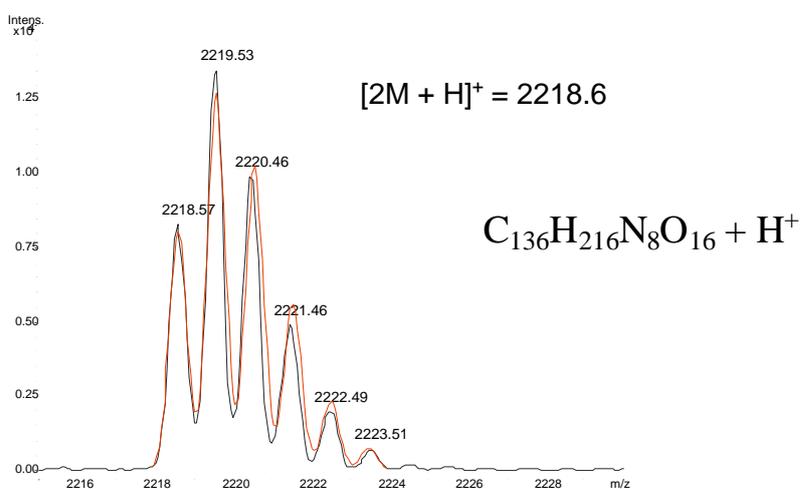
$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_1 [\text{M}_1+\text{Cl}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**Accurate Mass: MS** (ESI, positive/negative Ions)

$[\text{C}_x\text{H}_y\text{O}_z+\text{H}]^+ m/z (\text{calcd}) = 123.4567, m/z (\text{exp}) = 123.4576$

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited (exception:  $\text{MS}^n$  spectra) because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution.*

example:



#### abbreviations:

$\text{Mass}_x$ :  $m/z$  of the pseudomolecular ion

$\text{M}_x$ : number of the compound or its formula ( $\text{C}_x\text{H}_y\text{O}_z$ )

## 4. EI Mass spectrometry on the Autospec X

### experimental section:

EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were dissolved in dichloromethane and aluminium crucibles were filled with this solution and the solvent was evaporated. The aluminium crucibles were introduced by push rod if not otherwise noted. (Samples were introduced using the cold inlet system<sup>1</sup>). Ions were accelerated by 8 kV in EI mode. The mass axis was externally calibrated with PFK (perfluorokerosine) as calibration standard.

The spectra shown here are recorded and processed with the OPUS software (V3.6, Micromass 1998) by the accumulation and averaging of several single spectra.

Accurate mass measurements were performed in the high resolution mode with PFK as internal standard. Centroided spectra were used to determine the mass accuracy.

### specify (examples):

MS (EI, 70eV)

$m/z$  (%) = P (int) [Parent]<sup>+</sup>, F<sub>1</sub> (int) [Fragment 1]<sup>+</sup>, F<sub>2</sub> (int) [Fragment 2]<sup>+</sup>, ...

*Comment : In EI, the parent ion is a radical cation\*, the fragment ions can be either radical cations or cation, depending on the fragmentation. Please confirm the nature of your fragment ions.*

*\*Exception: In case the parent ion is a radical (e.g. NO), the parent ion is a cation.*

Accurate Mass: MS (EI, 70eV)

(C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)<sup>+</sup>  $m/z$  (calcd) = 123.4567,  $m/z$  (exp) = 123.4576

### abbreviations:

M<sub>x</sub>: number of the compound or it's formula (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)

P<sub>x</sub>:  $m/z$  of the parent ion

F<sub>x</sub>:  $m/z$  of the fragment ion

<sup>1</sup>Spross, J. JOVE-Journal of Visualized Experiments **2014**, 91

## 5. ESI and MALDI spectra on the Synapt G2Si (Q-IMS-TOF MS)

### experimental section:

Accurate Mass MALDI or nano-ESI measurements are performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters GmbH, Manchester, UK) in resolution mode, interfaced to a MALDI or nano-ESI ion source. Nitrogen serves both as the nebulizer gas and the dry gas for nano-ESI. Nitrogen is generated by a nitrogen generator NGM 11. Helium 5.0 is used as buffer gas in the IMS entry cell, nitrogen 5.0 is used for IMS separations. Argon serves as collision gas for MS/MS experiments. 1,3-dicyanobenzene is used as electron transfer reagent in ETD experiments. The MALDI source is equipped with a 2.5 kHz solid state Nd:YAG laser at a wavelength of 355 nm.

Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) mixed on a polished steel target with 1  $\mu\text{L}$  of matrix solution (either 50 mg/mL 2,5-DHB in 50% ACN, 0.1% TFA or saturated DCTB in methanol or 10 mg/mL CHCA in 50% ACN, 50% ethanol with 0.1% TFA).

Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) and introduced by static nano-ESI using *in-house* pulled glass emitters

### Choose relevant information (refer to print-out):

The mass axis was externally calibrated with (PEG or **red phosphorous**<sup>1</sup>) as calibration standard on the same target. (use for **MALDI experiments!**)

or

The mass axis was externally calibrated with fragment ions of GluFib as calibration standard. (use for **nano-ESI experiments!**)

or

The mass axis was internally calibrated with the doubly protonated GluFib ion or the protonated LeuEnk ion as internal calibration standard. (use for **nano-LC/nano-ESI experiments!**)

Scan accumulation and data processing was performed with MassLynx 4.1 (Waters GmbH, Manchester, UK) on a PC Workstation. The spectra shown here were generated by the accumulation and averaging of several single spectra (as given in print outs). Determination of exact masses were performed using centroided data. Drift spectra were visualized and selected with DriftScope v2.8.

### specify (examples, choose ionisation method):

**MS** (ESI/MALDI, positive ions)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

**MS** (ESI/MALDI, negative ions)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_1 [\text{M}_1+\text{Cl}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**MS/MS** (ESI/MALDI, P<sub>1</sub> ( $m/z$  XXX), positive ions)

$m/z (\%) = \text{P}_1 [\text{precursor}]^+, \text{D}_1 (\text{int}) [\text{daughter } 1]^+, \text{D}_2 (\text{int}) [\text{daughter } 2]^+, \dots$

**Accurate Mass: MS** (ESI/MALDI, positive/negative Ions)

$[\text{C}_x\text{H}_y\text{O}_z+\text{H}]^+ m/z (\text{calcd}) = 123.4567, m/z (\text{exp}) = 123.4576$

**Comment : In MALDI, the most matrix compounds generate adduct ions. However, when DCTB is used as a matrix compound, radical cations are generated!**  $\rightarrow m/z = \text{Mass}_1 [\text{M}_1]^{+\bullet}$

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited (exception: MS<sup>n</sup> spectra) because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution. (Compare example shown with Esquire 3000 or Ultraflex)*

**For details on nano-LC/nano-ESI-MS/MS, nano-ESI-MS/MS, Protein-nano-ESI-MS, and/or IMS experiments (e.g. proteomics) refer to the operator.**

*Lit.: <sup>1</sup>Sladkova, K., Houska, J., Havel, J. Rapid Comm. Mass Spectrom. 2009, 19, 3114-3118*

## 6. HPLC/TLC/Direct Infusion ESI mass spectrometry on the ZQ2000

### experimental section:

ESI mass spectra are recorded using a ZQ2000 single quadrupole mass spectrometer (Waters, Manchester, UK) equipped with a ESI source, operating with a spray voltage of 3.5 kV. Nitrogen served both as the nebulizer gas and the dry gas and is generated by a nitrogen generator NGM 11.

The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard.

**HPLC:** Samples were dissolved in *solvent* and introduced with a AllianceHT 2795 HPLC system consisting of an autosampler, degasser, binary pump and 996 photodiode array detector (Waters, Manchester, UK) using a C8 Symmetry column (length: 100 mm, diameter: 2.1 mm, particle size: 3,5  $\mu\text{m}$ ) with a gradient (in 10 min from 5% B to 95% B, back to 5% B in 0.2 min, total run time 25 min) at a flow rate of 400  $\mu\text{L}/\text{min}$ . HPLC solvent A consists of water and 0.1% formic acid, solvent B of acetonitrile and 0.1% formic acid. UV spectra are recorded in the range from 190 nm to 800 nm.

**TLC:** Samples are introduced using an in-house built TLC interface<sup>1,2</sup>, operated with a Hitachi L-6000 LC pump (isopropanol, flow rate 400  $\mu\text{L}/\text{min}$ ). *Add information of TLC separation.*

**Direct Infusion:** Samples are introduced using a syringe pump (*solvent and concentration*  $\rightarrow$  *operator*, flow rate: 10 or 40  $\mu\text{L}/\text{min}$ )

Scan accumulation and data processing was performed with MassLynx 4.1 (Waters, Manchester, UK) on a PC Workstation. The spectra shown here were generated by the accumulation and averaging of several single spectra (as given in print outs).

### specify (examples):

**MS** (ESI, positive ions)

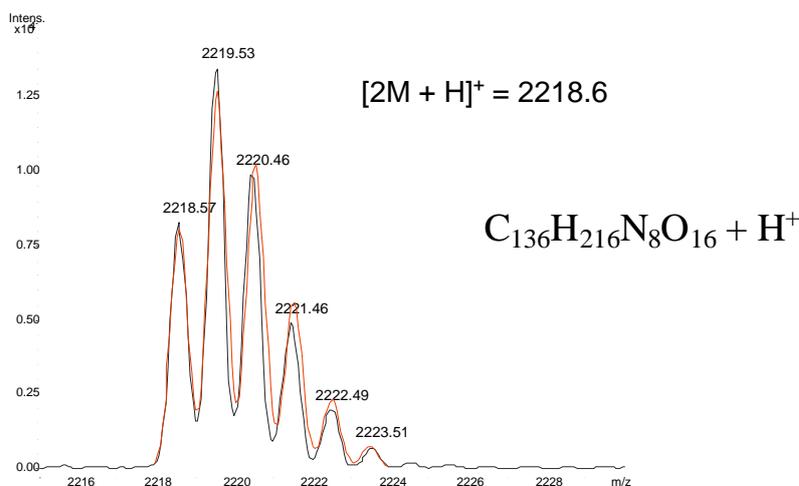
$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

**MS** (ESI, negative ions)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_1 [\text{M}_1+\text{Cl}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited (exception:  $\text{MS}^n$  spectra) because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution.*

example:



### abbreviations:

$\text{Mass}_x$ :  $m/z$  of the pseudomolecular ion

$\text{M}_x$ : number of the compound or it's formula ( $\text{C}_x\text{H}_y\text{O}_z$ )

<sup>1</sup> Luftmann, H Analytical and Bioanalytical Chemistry **2004**, 378, 964-968

<sup>2</sup> [https://www.uni-muenster.de/imperia/md/content/organisch\\_chemisches\\_institut2/massenspektrometrie/dgms-hl.pdf](https://www.uni-muenster.de/imperia/md/content/organisch_chemisches_institut2/massenspektrometrie/dgms-hl.pdf)

## 7. GC/MS on the Varian Saturn II (out of order)

### experimental section:

EI/CI GC/MS spectra were recorded using an Varian Saturn II GS/MS mass spectrometer equipped with an ion trap used with EI (70 eV) or CI with internal ionization.

The spectra shown here are recorded and processed with the Varian Saturn II Software Version 5.2 by the accumulation and averaging of several single spectra for each GC peak using background subtraction. The GC used a 25 m silica capillary column HP 5 MS (0.2 mm ID, 0.33  $\mu$ m film)<sup>1</sup>.

### specify (examples):

MS (EI, 70eV)

$m/z$  (%) = P (int) [Parent]<sup>+</sup>, F<sub>1</sub> (int) [Fragment 1]<sup>+</sup>, F<sub>2</sub> (int) [Fragment 2]<sup>+</sup>, ...

*Comment : In EI, the parent ion is a **radical cation**\*, the fragment ions can be either radical cations or cation, depending on the fragmentation. Please confirm the nature of your fragment ions.*

*\*Exception: In case the parent ion is a radical (e.g. NO), the parent ion is a cation.*

### abbreviations:

M<sub>x</sub>: number of the compound or it's formula (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)

P<sub>x</sub>:  $m/z$  of the parent ion

F<sub>x</sub>:  $m/z$  of the fragment ion

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<sup>1</sup> Please ask a GCMS operator for the actual column your samples have been separated with!

## 8. MALDI TOF Mass spectrometry on the Voyager DE (out of order)

### experimental section:

Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) mixed on a steel target with 1  $\mu\text{L}$  of matrix solution (either 50 mg/mL 2,5-DHB in 50% ACN, 0,1% TFA or saturated DCTB in methanol). MALDI TOF mass spectra were recorded with a linear Voyager™ DE Instrument (PE Biosystems GmbH, Weiterstadt, Germany) mounted with a 1.2m flight tube. Ionisation was achieved using a LTB nitrogen laser MNL 100 (337 nm beam wavelength, 3ns pulse width, 3 Hz repetition rate). Depending on the mass range the ions were accelerated at 15 to 25 kV in the positive or negative ion mode. Maximum resolution achieved with this instrument is approx. 2000.

The Instrument Default Calibration was used for calibrating the mass axis.

or

The mass axis was externally calibrated with (PEG or **fullerenes**) as calibration standard on the same target.

or

The mass axis was internally calibrated with ... as internal calibration standard.

The spectra are recorded with the Voyager Instrument Control Software (V 5.10) by accumulation and averaging of ... single laser shots. PE Data Explorer software V4.0.0.0 was used for processing the spectra.

### specify (example):

MS (MALDI TOF, positive ions, Matrix, AcceleratingVoltage, Nr.of summed Spectra)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

MS (MALDI TOF, negative ions, Matrix, AcceleratingVoltage, Nr.of summed Spectra)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**Comment : In MALDI, the most matrix compounds generate adduct ions. However, when DCTB is used as a matrix compound, radical cations are generated!  $\rightarrow m/z = \text{Mass}_1 [\text{M}_1]^{\bullet+}$**

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution (compare example shown with Ultraflex).*

### abbreviations:

Mass<sub>x</sub>:  $m/z$  of the pseudomolecular ion

M<sub>x</sub>: number of the compound or it's formula (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>)

## 9. ESI and MALDI spectra on the APEX III (FT-ICR MS) (out of order)

### experimental section:

**ESI:** Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) and introduced by static nano-ESI using *in-house* pulled glass emitters

**MALDI:** Samples were dissolved in *solvent* [containing e.g. sodium perchlorate or similar compound to enhance adduct formation] (refer to print out) mixed on a polished steel target with 1  $\mu\text{L}$  of matrix solution (either 50 mg/mL 2,5-DHB in 50% ACN, 0.1% TFA or saturated DCTB in methanol or 10 mg/mL CHCA in 50% ACN, 50% ethanol with 0.1% TFA).

ESI or MALDI experiments were performed using a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer APEX III (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T, 160 mm bore superconducting magnet (Bruker Analytik GmbH – Magnetics, Karlsruhe, Germany), infinity cell, and interfaced to an APOLLO nano-ESI or Scout 100 MALDI ion source. Nitrogen 5.0 served both as the nebulizer gas and the dry gas for ESI. MALDI ionisation was achieved using a nitrogen laser (337 nm beam wavelength). Argon served as cooling gas in the infinity cell and collision gas for  $\text{MS}^n$  experiments.

Scan accumulation and fourier transformation were performed with XMASS NT (7.08) on a PC Workstation, for further data processing DataAnalysis™ 3.4 was used.

### specify (examples):

**MS** (ESI, positive ions)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

**MS** (ESI, negative ions)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**MS/MS** (ESI,  $\text{P}_1$  ( $m/z$  XXX), positive ions)

$m/z$  (%) =  $\text{P}_1$  [precursor]<sup>+</sup>,  $\text{D}_1$  (int) [daughter 1]<sup>+</sup>,  $\text{D}_2$  (int) [daughter 2]<sup>+</sup>, ...

**$\text{MS}^3$**  (ESI,  $\text{P}_1$  ( $m/z$  XXX)  $\rightarrow$   $\text{P}_2$  ( $m/z$  YYY), positive ions)

$m/z$  (%) =  $\text{P}_2$  [precursor]<sup>+</sup>,  $\text{D}_1$  (int) [daughter 1]<sup>+</sup>,  $\text{D}_2$  (int) [daughter 2]<sup>+</sup>, ...

**MS** (MALDI TOF, positive ions, Matrix)

$m/z = \text{Mass}_1 [\text{M}_1+\text{H}]^+, \text{Mass}_1 [\text{M}_1+\text{Na}]^+, \text{Mass}_1 [\text{M}_1+\text{K}]^+, \text{Mass}_2 [\text{M}_2+\text{H}]^+, \dots$

**MS** (MALDI TOF, negative ions, Matrix)

$m/z = \text{Mass}_1 [\text{M}_1-\text{H}]^-, \text{Mass}_2 [\text{M}_2-\text{H}]^-, \dots$

**Accurate Mass: MS** (ESI/MALDI, positive/negative Ions)

$[\text{C}_x\text{H}_y\text{O}_z+\text{H}]^+ m/z$  (calcd) = 123.4567,  $m/z$  (exp) = 123.4576

**Comment : In MALDI, the most matrix compounds generate adduct ions. However, when DCTB is used as a matrix compound, radical cations are generated!  $\rightarrow m/z = \text{Mass}_1 [\text{M}_1]^{+\bullet}$**

*For soft ionisation techniques relative (!) intensities in the spectra should not be cited (exception:  $\text{MS}^n$  spectra) because they are not reproducible in substance mixtures and on different MS instruments. If the isotopic cluster of a compound shall be cited as a proof for the elemental composition of a special compound, relative ion abundances have to be given as values or (better) the cluster may be depicted in comparison with the calculated isotopic distribution (compare example shown with Ultraflex or Esquire 3000).*