m/z = 120		M	M (%)	M+1 (%)	M+2 (%)
	$C_2H_4N_2O_4$	120,017107	100	3,15	0,84
	$C_2H_6N_3O_3$	120,040916	100	3,52	0,65
	$C_3H_{12}N_4O$	120,101111	100	5,00	0,31
	$C_4H_{12}N_2O_2$	120,089878	100	5,36	0,52
	$C_6H_6N_3$	120,056172	100	7,72	0,26
	C_9H_{12}	120,093900	100	9,92	0,44

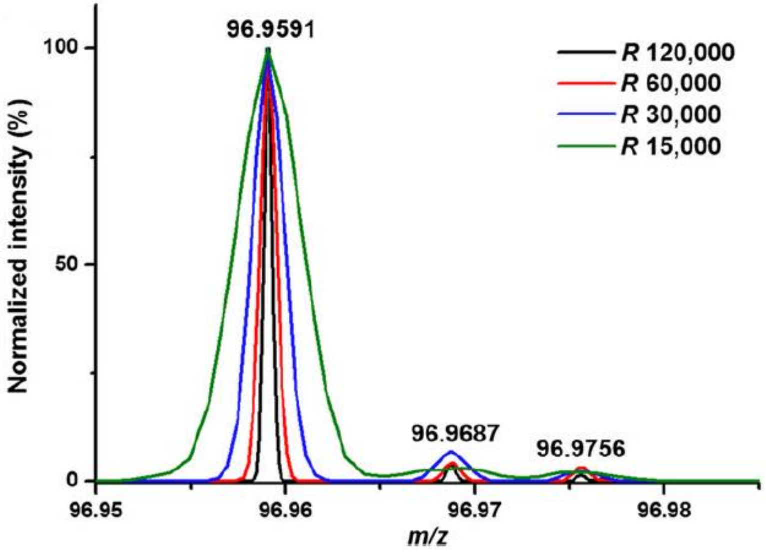
How much R is needed? R>30000

Requirement for small molecules: Accuracy < 10ppm
(measured-calculated)/calculated*10^6

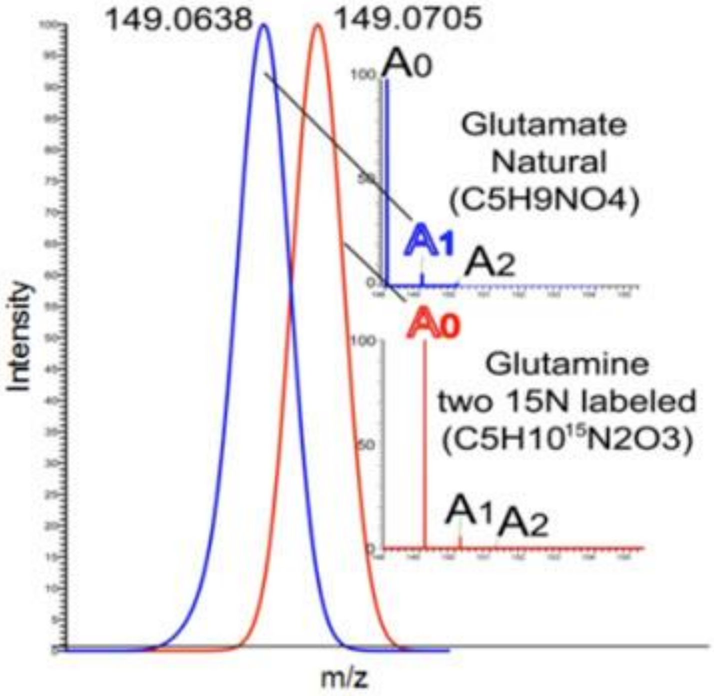
What is the accuracy of the measurement if
M=120.091375 measured?

Alternative of elemental analysis: characterises the individual components, not the sample in whole (Pro/Con)

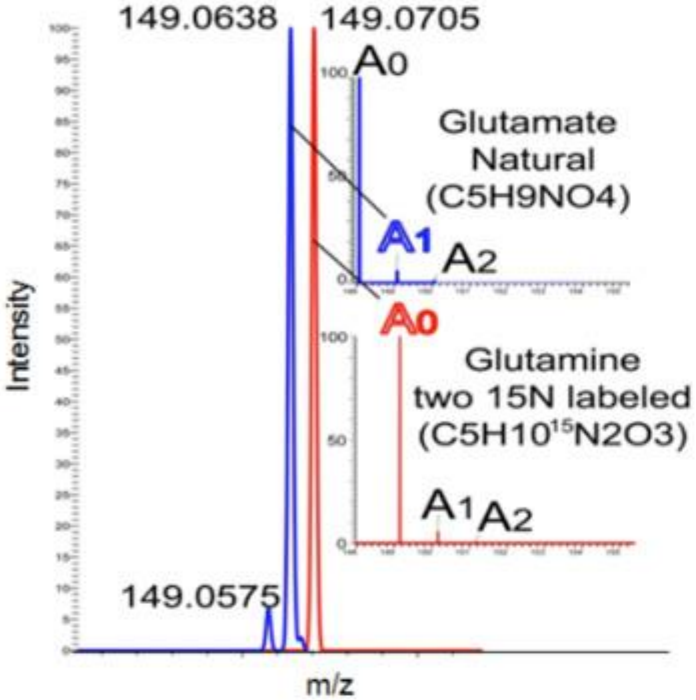
HRMS: R>10000



R=20,000, average QTOF analyzer



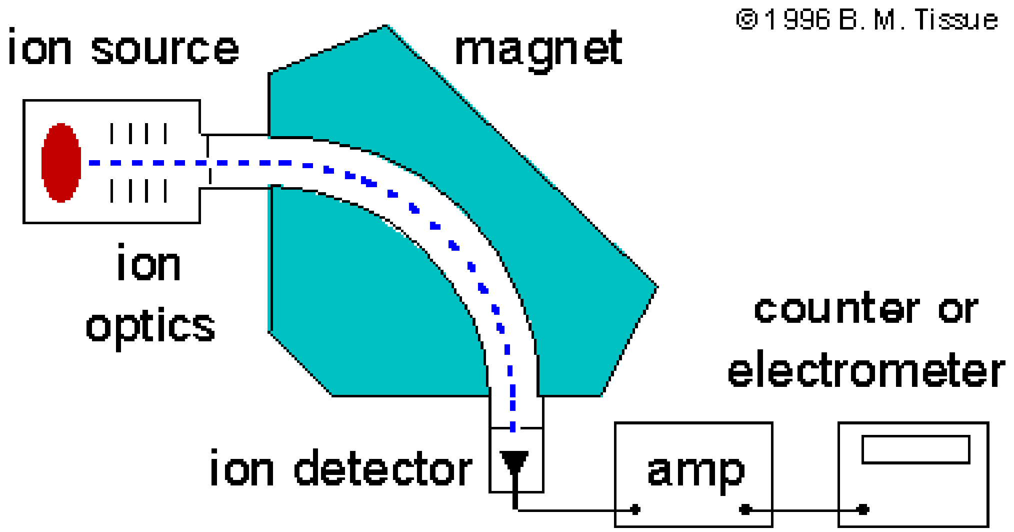
R=100,000, Orbitrap analyzer



Analyzers

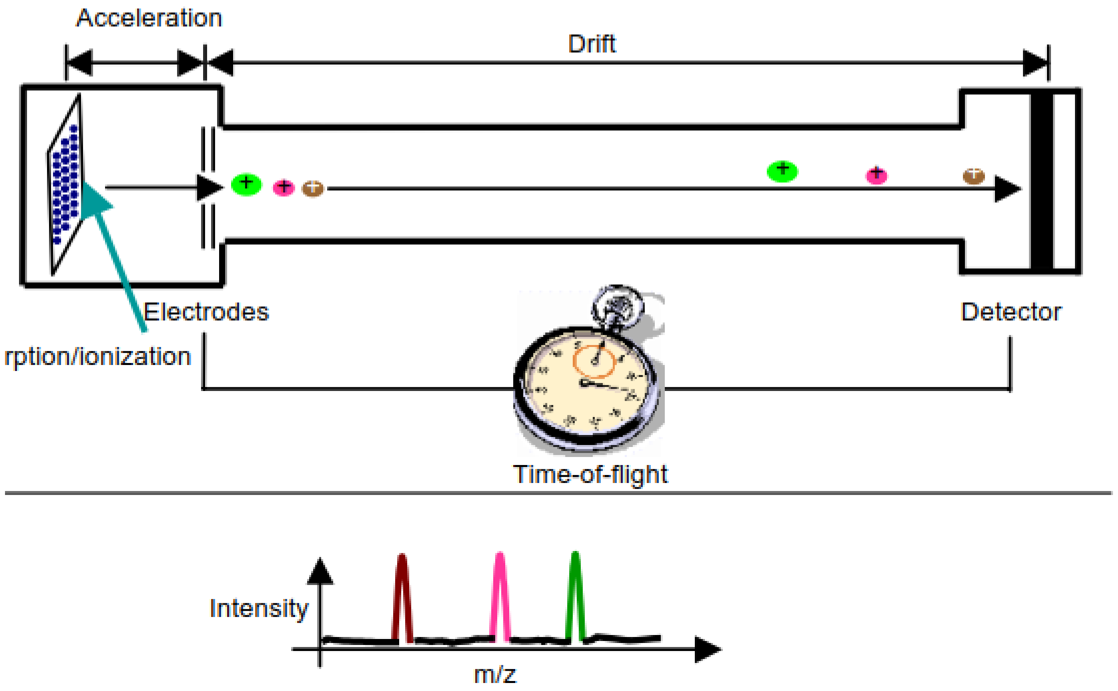
Sector instruments

A sector field mass analyzer uses a static electric and/or magnetic field to affect the path and/or velocity of the charged particles in some way. As shown above, sector instruments bend the trajectories of the ions as they pass through the mass analyzer, according to their mass-to-charge ratios, deflecting the more charged and faster-moving, lighter ions more. The analyzer can be used to select a narrow range of m/z or to scan through a range of m/z to catalog the ions present.



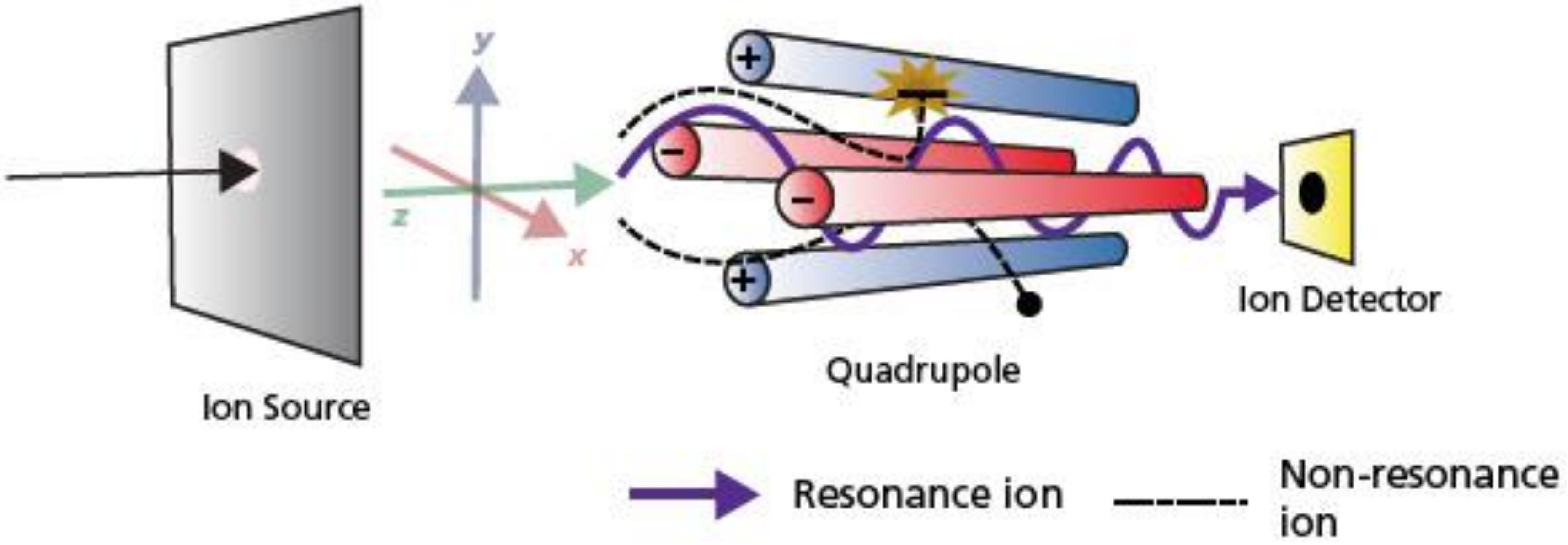
Time-of-flight

The time-of-flight (TOF) analyzer uses an electric field to accelerate the ions through the same potential, and then measures the time they take to reach the detector. If the particles all have the same charge, their kinetic energies will be identical, and their velocities will depend only on their masses. Ions with a lower mass will reach the detector first.



Quadrupole mass filter

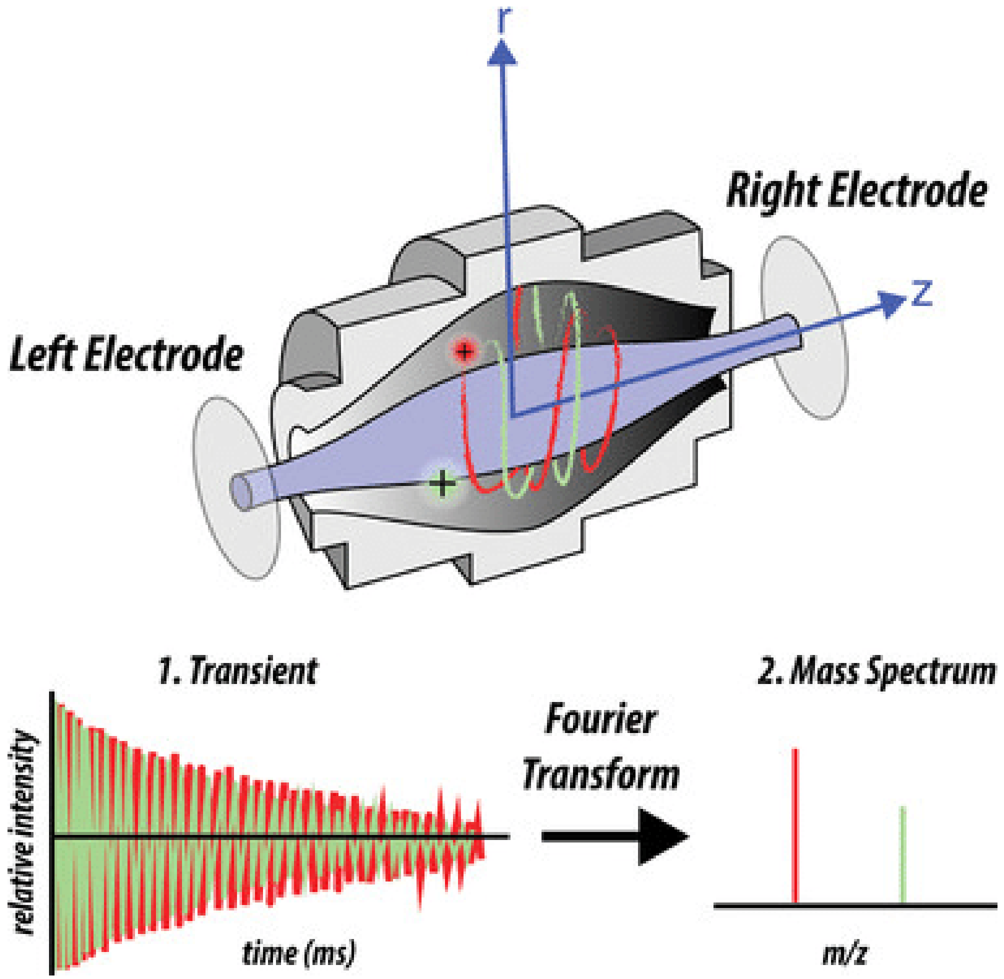
Quadrupole mass analyzers use oscillating electrical fields to selectively stabilize or destabilize the paths of ions passing through a radio frequency (RF) quadrupole field created between 4 parallel rods. Only the ions in a certain range of mass/charge ratio are passed through the system at any time, but changes to the potentials on the rods allow a wide range of m/z values to be swept rapidly, either continuously or in a succession of discrete hops.



Orbitrap

Orbitrap instruments are similar to Fourier transform ion cyclotron resonance mass spectrometers. Ions are electrostatically trapped in an orbit around a central, spindle shaped electrode. The electrode confines the ions so that they both orbit around the central electrode and oscillate back and forth along the central electrode's long axis. This oscillation generates an image current in the detector plates which is recorded by the instrument. The frequencies of these image currents depend on the mass-to-charge ratios of the ions. Mass spectra are obtained by Fourier transformation of the recorded image currents.

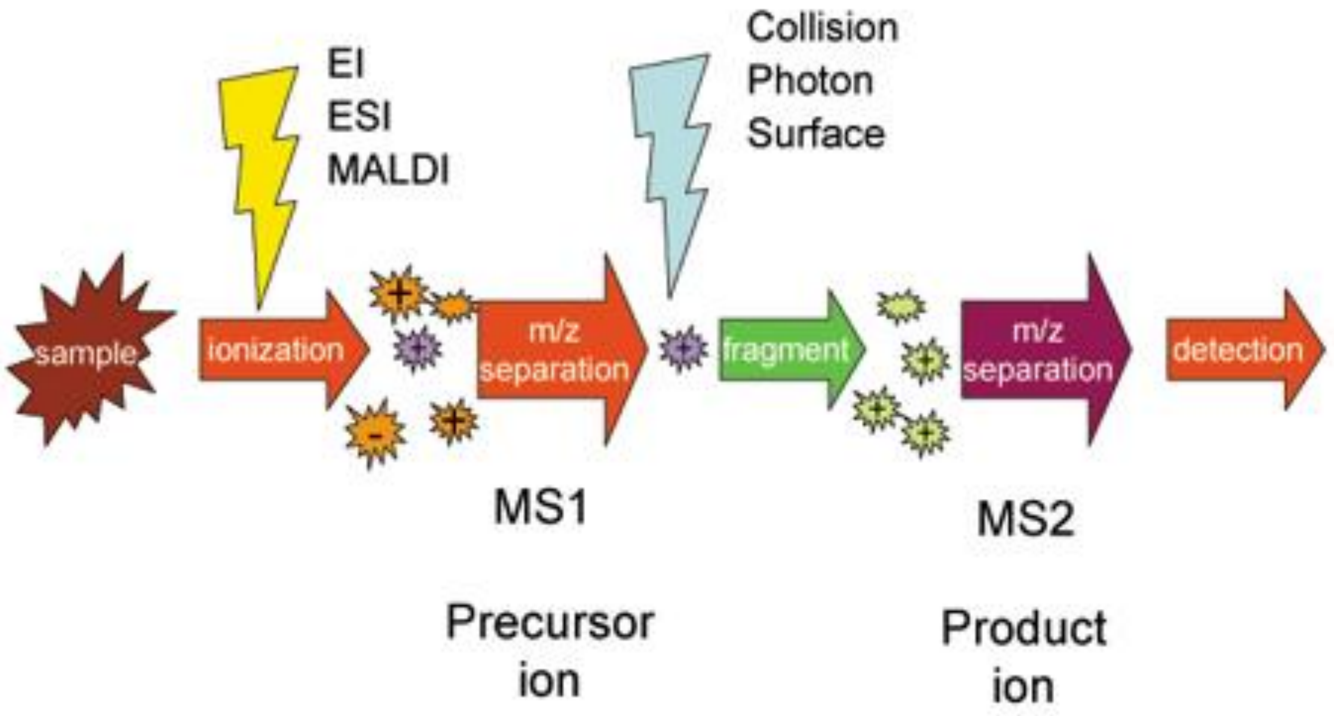
Orbitraps have a high mass accuracy, high sensitivity and a good dynamic range.



Ion traps

The quadrupole ion trap works on the same physical principles as the quadrupole mass analyzer, but the ions are trapped and sequentially ejected. Ions are trapped in a mainly quadrupole RF field, in a space defined by a ring electrode (usually connected to the main RF potential) between two endcap electrodes (typically connected to DC or auxiliary AC potentials). The sample is ionized either internally (e.g. with an electron or laser beam), or externally, in which case the ions are often introduced through an aperture in an endcap electrode.

MS^n is possible



Type	Resolving Power (FWHM)
FT-ICR-MS	1,000,000
FT-Orbitrap	500000-1000000
High-Res-TOF	60,000
TOF	10,000
Quadrupole / IonTrap in UltraZoom mode	10,000
Quadrupole / Iontrap	1,000

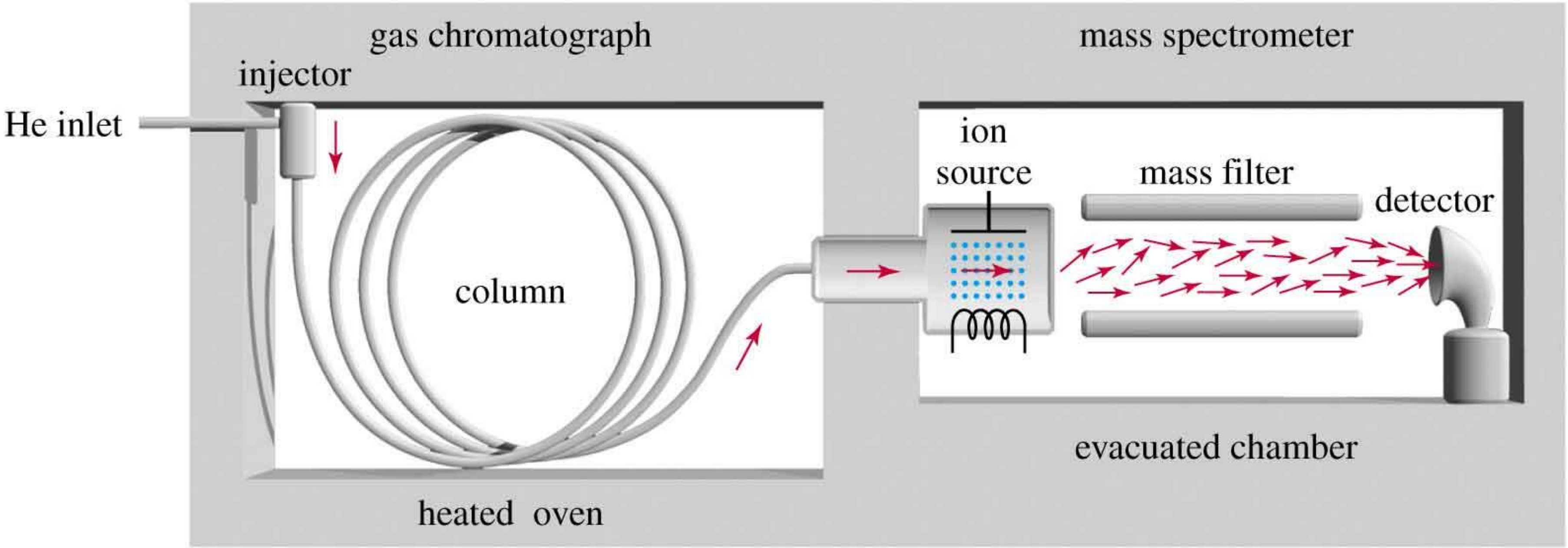
MS characteristics

- **Extremely** sensitive
- Broad range (40- 100kDa)
- reproducible
- Whatever phase
- Easy combination with chromatography
- Quantitation is possible

>100 spectrometers, no universal instrument

GC-MS

For high volatile molecules



SWOT analysis

Strength

- high sensitivity (10^{-15}g)
- fast (10 spektrum/s)
- efficient (simple sample preparation)
- easily coupled with chromatography
- quantitative and qualitative information

Weaknesses

- expensive (ca 100 000 Euro)
- needs special knowhow
- interpretation is difficult

SWOT analysis

Opportunities

- verification (data base)
- macromolecules (proteomics)
- broad field application

Threats

- not every compound is detectable
- sensitivity is heavily dependent on compound
- precaution is needed when used together with chromatography

General rules

Nitrogen rule

If M is even, then number of N is even (CHNOSF molecules).

Fragmentation rules

chain branching: possible positions for cleavage

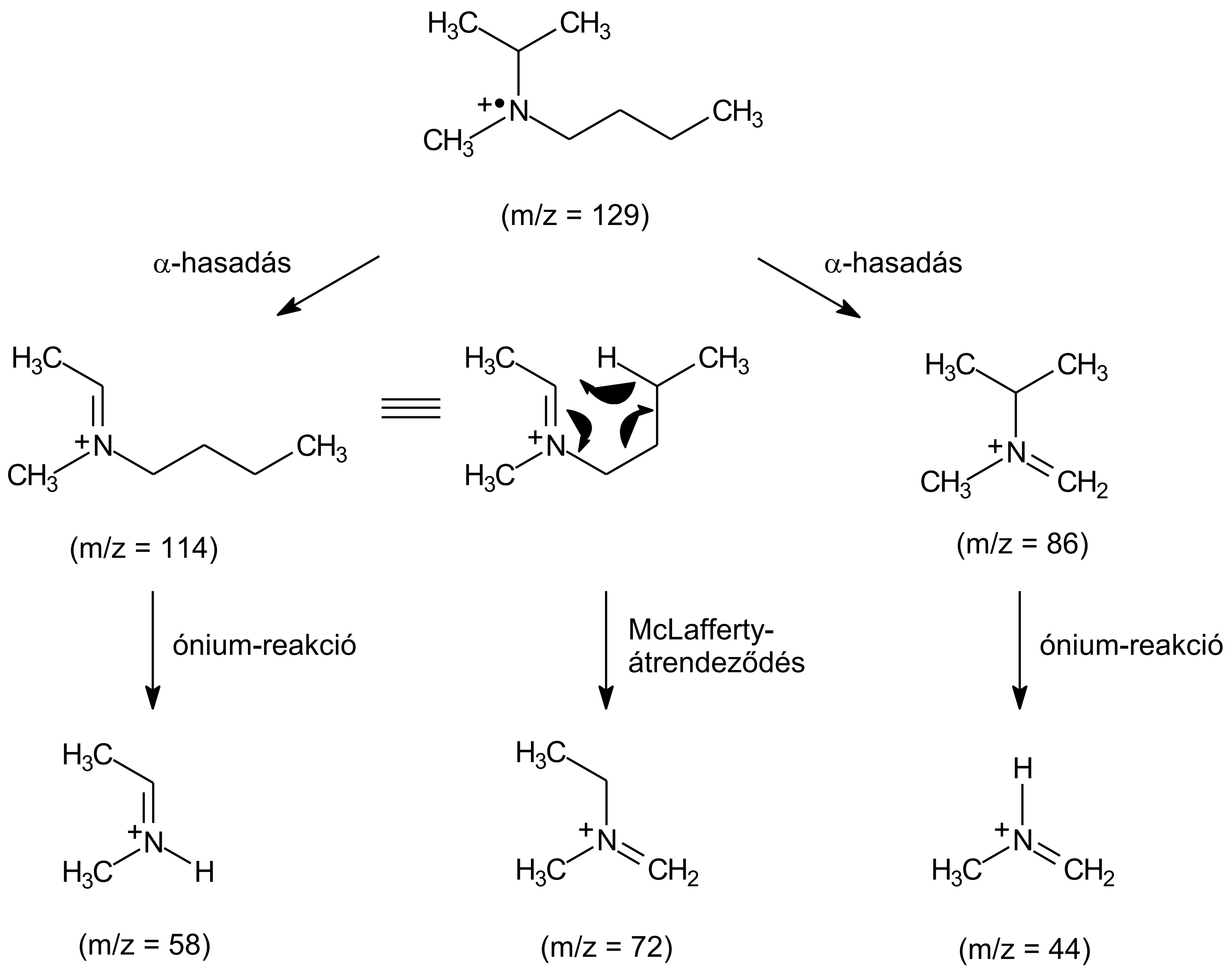
stable molecules tends to leave (CH_2=CH_2, CH≡CH, CO, CO_2, HCl, H_2O, N_2, NO_2 etc)

formation of stable cations (allylic, formyl, acetyl, tropilium, etc)

Fragmentation is unique to every compound
Depends heavily on instrument/settings

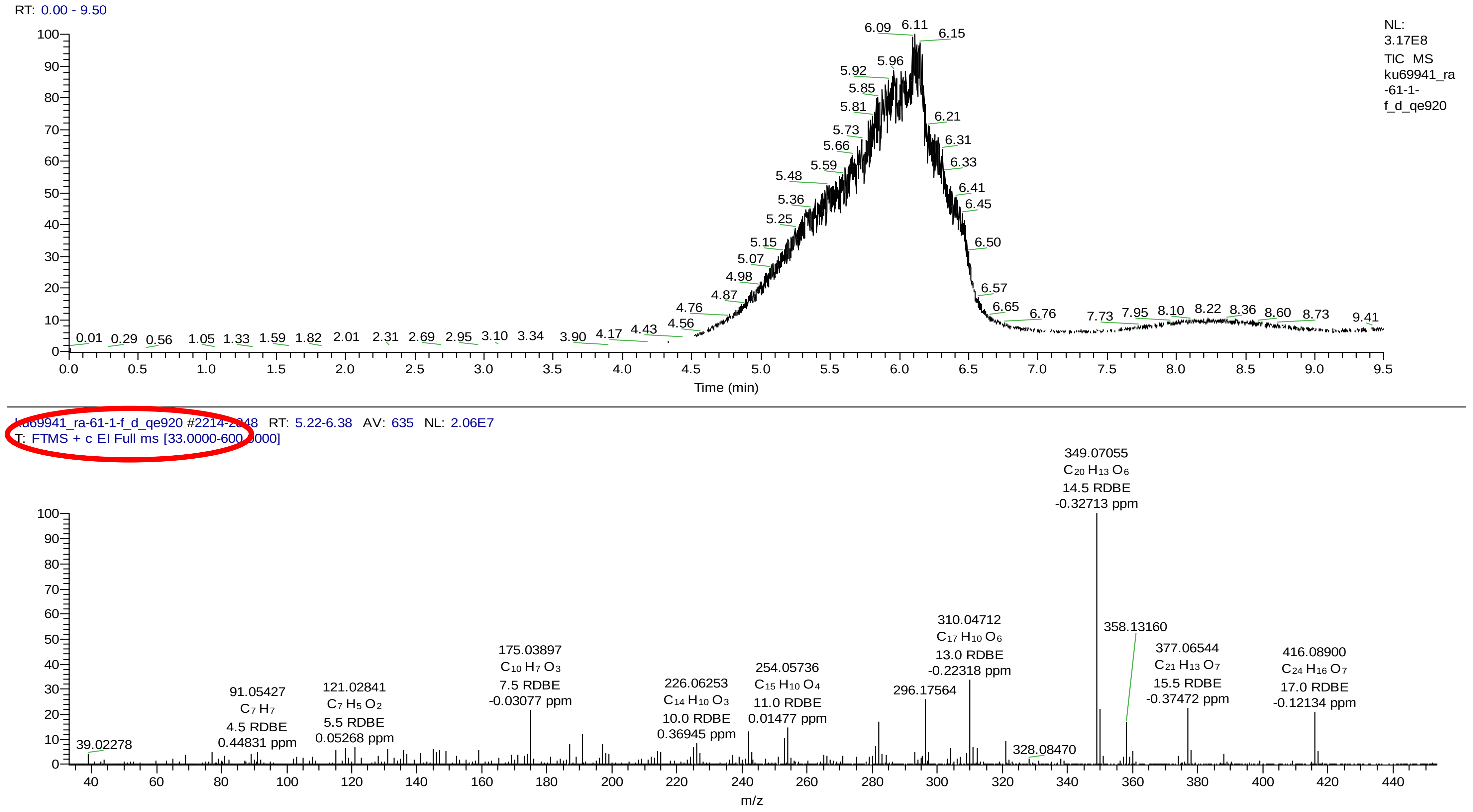
A structure can be verified or excluded based on the fragmentation pattern, but not elucidated (there are exceptions)
„The spectrum is in accordance with the suggested structure”.

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Instrumental_Analysis/Mass_Spectrometry/Mass_Spec/Mass_Spectrometry_-_Fragmentation_Patterns



(m/z = 129)
α-hasadás
α-hasadás
(m/z = 114)
(m/z = 86)
ónium-reakció
McLafferty-átrendeződés
ónium-reakció
(m/z = 58)
(m/z = 72)
(m/z = 44)

ku69941_ra-61-1-f_d_qe920 09/23/19 14:15:24 Hazai L./ Pallag E.



Analysis Info

Analysis Name	LS-III-156_pos_000001.d	Acquisition Date	7/22/2011 10:54:16 AM
Method	XMASS_Method	Operator	FTMS_USER
Sample Name:	LS-III-156_pos	Instrument	apex-Qe
	LS-III-156_pos: in 1:1 THF:MeOH w/ NaCl.		

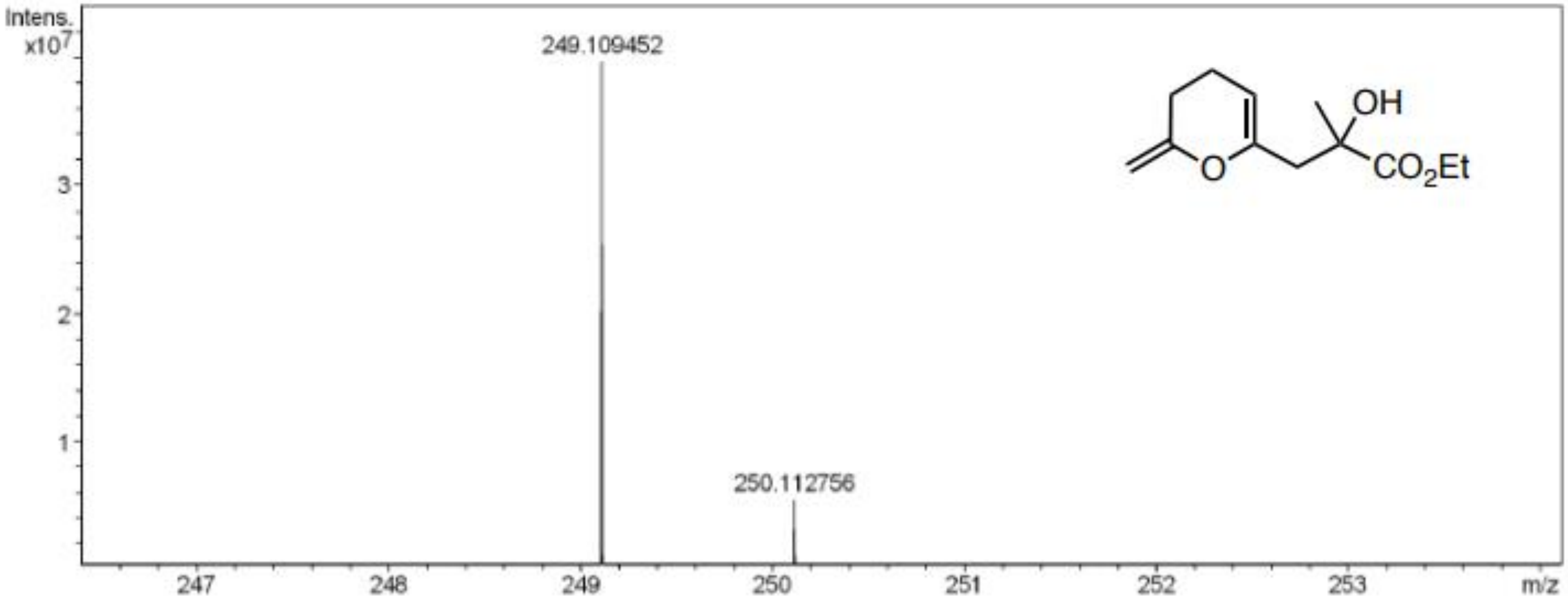
Acquisition Parameter

Sample: LS-III-156

Exact Mass of ($C_{12}H_{18}O_4$)Na^+ = 249.109730u

Observed Mass = 249.109452u

Difference = -1.1 ppm



http://chemistry.syr.edu/totah/che575/support/3a1/3-3.MS.pdf ionization technique/method

peak assignment

MS (EI, 75 eV): m/z 102 (M^+, 1%), 87 (16), 74 (64), 71 (50), 59 (22), 43 (100) ....

mass

height of peak relative to base peak

ionization method

molecular ion observed

HRMS (ESI): calcd for $C_{12}H_{18}O_4Na$ ($[M+Na]^+$) 249.1097; found 249.1094.

chemical formula of (quasi) molecular ion

exact mass calculated

mass found