

Espectrometria de Massas



- Espectrometria de massas é a técnica analítica que estuda as massas de átomos ou moléculas ou de fragmentos de moléculas.

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1. Tabela Periódica dos elementos



| | | | | | | | | | | | | | | | | | | | |
|---------------------|---------------------|---------------------|------------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|------------------|-------------------|--------------------|--------------------|--------------------|---------------------|-------------------|-------------------|--------------------|--------------------|
| IA | | | | | | | | | | | | | | | | | | VIII A | |
| 1 | | | | | | | | | | | | | | | | | | 2 | |
| H | | | | | | | | | | | | | | | | | | He | |
| Hydrogen 1.0079 | | | | | | | | | | | | | | | | | | Helium 4.0026 | |
| IIA | | | | | | | | | | | | | | | | | | VIII B | |
| 3 | 4 | | | | | | | | | | | | | | | | | 5 | 6 |
| Li | Be | | | | | | | | | | | | | | | | | B | C |
| Lithium 6.941 | Beryllium 9.0122 | | | | | | | | | | | | | | | | | Boron 10.811 | Carbon 12.011 |
| 11 | 12 | | | | | | | | | | | | | | | | | 13 | 14 |
| Na | Mg | | | | | | | | | | | | | | | | | Al | Si |
| Sodium 22.990 | Magnesium 24.305 | | | | | | | | | | | | | | | | | Aluminum 26.982 | Silicon 28.086 |
| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | Rb | Sr |
| Potassium 39.098 | Calcium 40.078 | Scandium 44.956 | Titanium 47.867 | Vanadium 50.942 | Chromium 51.996 | Manganese 54.938 | Iron 55.845 | Cobalt 58.933 | Nickel 58.693 | Copper 63.546 | Zinc 65.409 | Gallium 69.723 | Germanium 72.64 | Arsenic 74.922 | Selenium 78.96 | Bromine 79.904 | Krypton 83.798 | Rubidium 85.468 | Strontium 87.62 |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | Cesium 132.91 | Barium 137.33 |
| Rubidium 85.468 | Strontium 87.62 | Yttrium 88.906 | Zirconium 91.224 | Niobium 92.906 | Molybdenum 95.94 | Technetium (98) | Ruthenium 101.07 | Rhodium 102.91 | Palladium 106.42 | Silver 107.87 | Cadmium 112.41 | Indium 114.82 | Tin 118.71 | Antimony 121.76 | Tellurium 127.60 | Iodine 126.90 | Xenon 131.29 | Cesium 132.91 | Barium 137.33 |
| 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | Francium (223) | Radium (226) |
| Cesium 132.91 | Barium 137.33 | Lanthanum 138.91 | Hafnium 178.49 | Tantalum 180.95 | Tungsten 183.84 | Rhenium 186.21 | Osmium 190.23 | Iridium 192.22 | Platinum 195.08 | Gold 196.97 | Mercury 200.59 | Thallium 204.38 | Lead 207.2 | Bismuth 208.98 | Polonium (209) | Astatine (210) | Radon (222) | Francium (223) | Radium (226) |
| 87 | 88 | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | | 114 | | | | | | |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Uun | Uuu | Uub | | Uuq | | | | | | |
| Francium (223) | Radium (226) | Actinium (227) | Rutherfordium (261) | Dubnium (262) | Seaborgium (266) | Bohrium (264) | Hassium (277) | Meitnerium (268) | (281) | (272) | (285) | | (289) | | | | | | |

Atomic number →

6

Symbol →

C

Name (IUPAC) →

Carbon

Atomic mass →

12.011

Chemical Abstracts Service group notation →



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Átomos



Número atômico (Z) →

Símbolo →

Nome (IUPAC) →

Massa atômica (A) →

| |
|--------|
| 6 |
| C |
| Carbon |
| 12.011 |

Elementos são feitos de átomos.

Átomos consistem de um **núcleo denso** e positivamente carregado, contendo *prótons* e *neutros*, rodeado por uma nuvem eletrônica contendo *elétrons* negativamente carregados.

Nuvem eletrônica

Núcleo

Partículas fundamentais



Número atômico (Z) →

Símbolo →

Nome (IUPAC) →

Massa atômica (A) →

| |
|--------|
| 6 |
| C |
| Carbon |
| 12.011 |

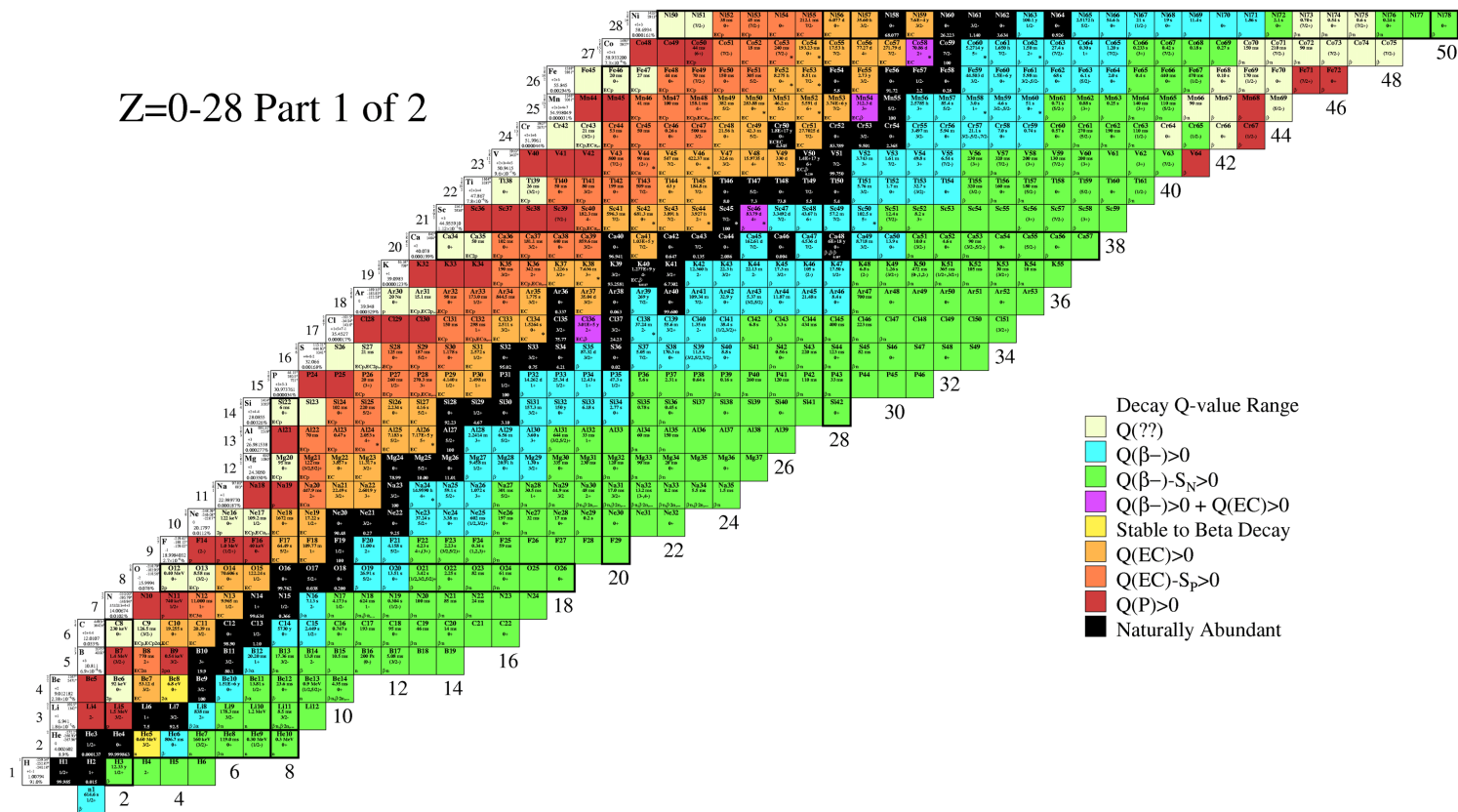
A quantidade de *neutrons* no núcleo pode ser obtida subtraindo a quantidade de *prótons* (Z) da massa atômica (A)

O número atômico (Z) corresponde a quantidade de *prótons* no núcleo, e normalmente equivale a quantidade de *elétrons* na nuvem eletrônica que rodeia o núcleo.

Table of Isotopes (1999)



Z=0-28 Part 1 of 2



Isótopos



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| | | | | | | | | | | | | | | |
|---|---|---|---|---|--|-------------------------------------|--------------------------------------|-----------------------------|--------------------------------------|---|---|---|--|---|
| 6 | 7 | 8 | ² ₆ O -218.79 ^o -182.95 ^o -118.56 ^o -2 15.9994 0.078% | O12 0.40 MeV 0+ 2p | O13 8.58 ms (3/2-) ECp | O14 70.606 s 0+ EC | O15 122.24 s 1/2- EC | O16 0+ 99.762 | O17 5/2+ 0.038 | O18 0+ 0.200 | O19 26.91 s 5/2+ β ⁻ | O20 13.51 s 0+ β ⁻ | O21 3.42 s (1/2,3/2,5/2)+ β ⁻ | O22 2.25 s 0+ β ⁻ |
| | | | ² ₅ N -210.00 ^o -195.79 ^o -146.94 ^o ±1±2±3±4±5 14.00674 0.0102% | N10 740 keV 1/2+ p | N11 11.000 ms 1+ EC3α | N12 9.965 m 1/2- EC | N13 1+ 99.634 | N14 1/2- 0.366 | N15 2- β ⁻ α | N16 4.173 s 1/2- β ⁻ n | N17 624 ms 1- β ⁻ n,β ⁻ α,... | N18 0.304 s (1/2-) β ⁻ n | N19 100 ms β ⁻ n | N20 85 m β ⁻ n |
| | | | ² ₄ C 44921 ^o 36424 ^o +2+44 12.0107 0.033% | C8 230 keV 0+ ECp,ECp2α | C9 126.5 ms (3/2-) EC | C10 19.255 s 0+ EC | C11 20.39 m 3/2- EC | C12 0+ 98.90 | C13 1/2- 1.10 | C14 5730 y 0+ β ⁻ | C15 2.449 s 1/2+ β ⁻ | C16 0.747 s 0+ β ⁻ n | C17 193 ms β ⁻ n | C18 95 ms 0+ β ⁻ n |



Isótopos



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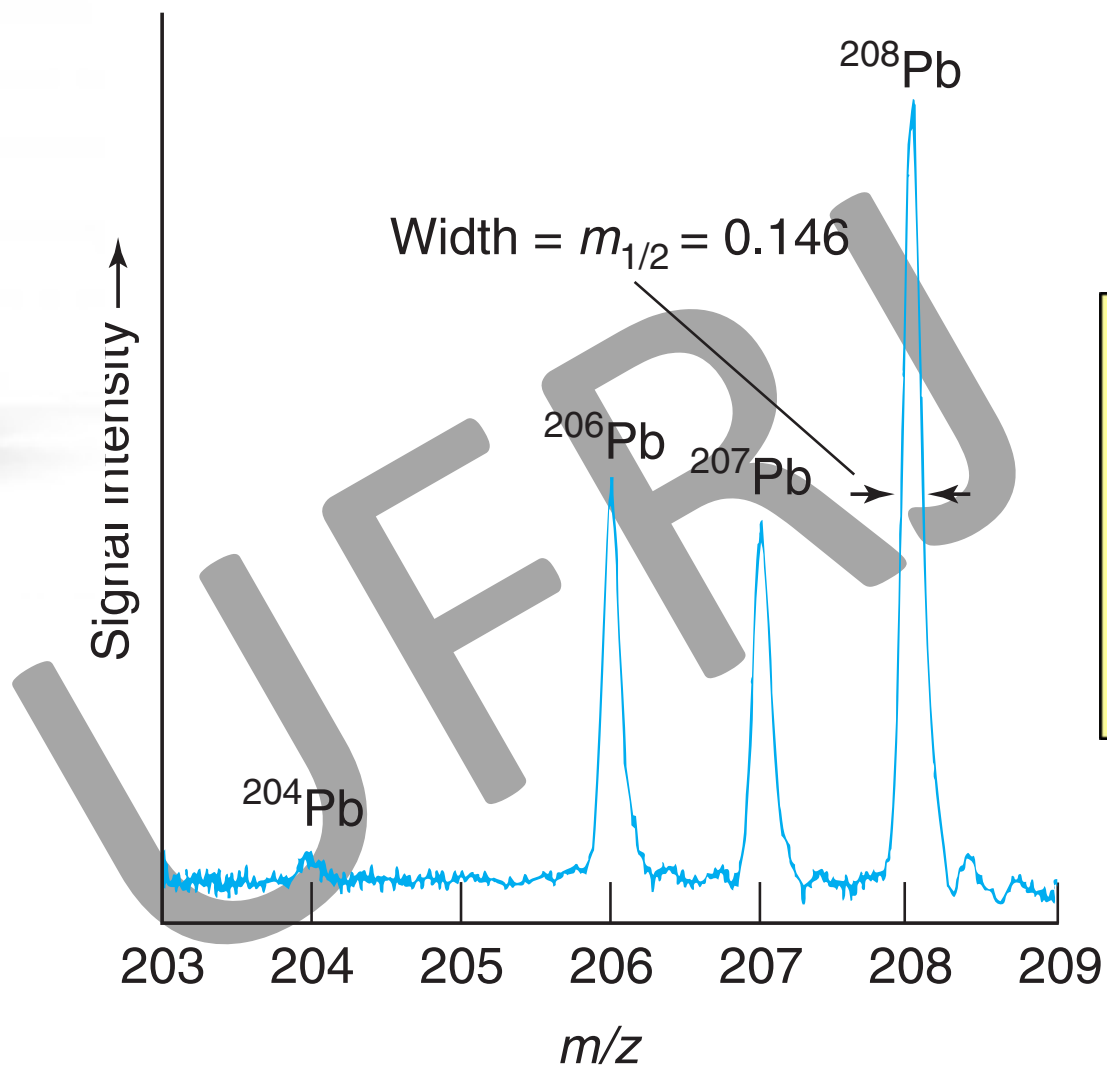
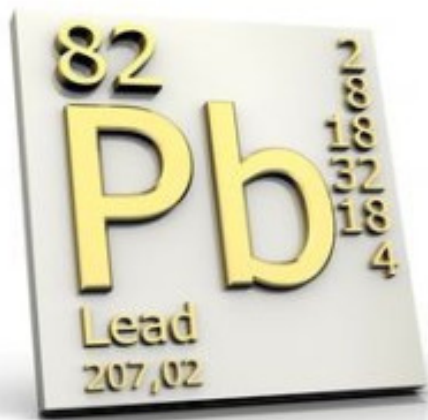
| Element | Mass number | Mass (Da) ^a | Abundance (atom %) ^b | Element | Mass number | Mass (Da) ^a | Abundance (atom %) ^b |
|----------|-------------|------------------------|---------------------------------|---------|-------------|------------------------|---------------------------------|
| Proton | 1 | 1.007 276 467 | — | Cl | 35 | 34.968 85 | 75.78 |
| Neutron | 1 | 1.008 664 916 | — | | 37 | 36.965 90 | 24.22 |
| Electron | — | 0.000 548 580 | — | Ar | 36 | 35.967 55 | 0.336 |
| H | 1 | 1.007 825 | 99.988 | | 38 | 37.962 73 | 0.063 |
| | 2 | 2.014 10 | 0.012 | | 40 | 39.962 38 | 99.600 |
| B | 10 | 10.012 94 | 19.9 | Fe | 54 | 53.939 61 | 5.845 |
| | 11 | 11.009 31 | 80.1 | | 56 | 55.934 94 | 91.754 |
| C | 12 | 12(exact) | 98.93 | | 57 | 56.935 40 | 2.119 |
| | 13 | 13.003 35 | 1.07 | | 58 | 57.933 28 | 0.282 |
| N | 14 | 14.003 07 | 99.632 | Br | 79 | 78.918 34 | 50.69 |
| | 15 | 15.000 11 | 0.368 | | 81 | 80.916 29 | 49.31 |
| O | 16 | 15.994 91 | 99.757 | I | 127 | 126.904 47 | 100 |
| | 17 | 16.999 13 | 0.038 | Hg | 196 | 195.965 81 | 0.15 |
| | 18 | 17.999 16 | 0.205 | | 198 | 197.966 75 | 9.97 |
| F | 19 | 18.998 40 | 100 | | 199 | 198.968 26 | 16.87 |
| Si | 28 | 27.976 93 | 92.230 | | 200 | 199.968 31 | 23.10 |
| | 29 | 28.976 49 | 4.683 | | 201 | 200.970 29 | 13.18 |
| | 30 | 29.973 77 | 3.087 | | 202 | 201.970 63 | 29.86 |
| P | 31 | 30.973 76 | 100 | | 204 | 203.973 48 | 6.87 |
| S | 32 | 31.972 07 | 94.93 | Pb | 204 | 203.973 03 | 1.4 |
| | 33 | 32.971 46 | 0.76 | | 206 | 205.974 45 | 24.1 |
| | 34 | 33.967 87 | 4.29 | | 207 | 206.975 88 | 22.1 |
| | 36 | 35.967 08 | 0.02 | | 208 | 207.976 64 | 52.4 |



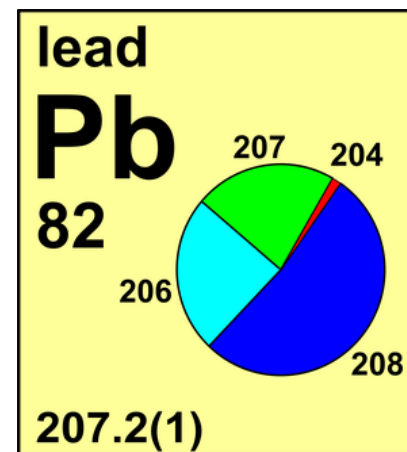
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Espectro de Massas



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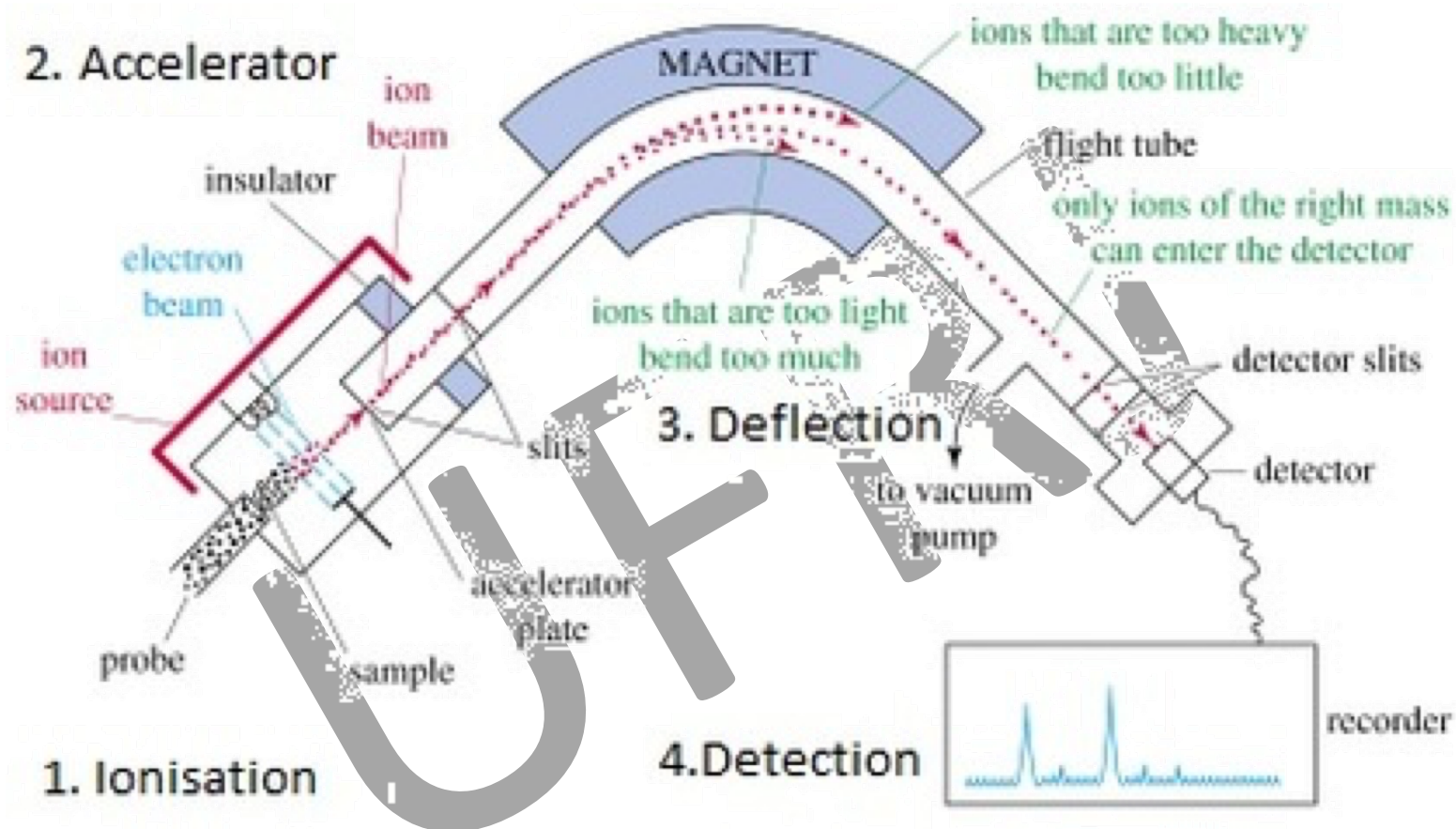


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Espectrômetro de Massas



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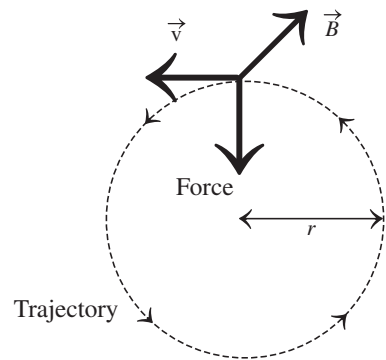
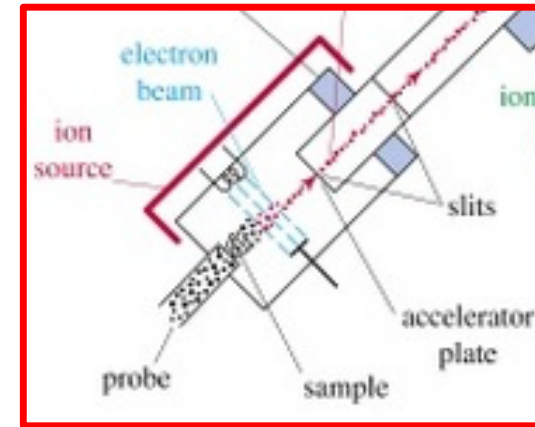
Espectrômetro de Massas



$$\frac{1}{2}mv^2 = zeV \Rightarrow v = \sqrt{\frac{2zeV}{m}}$$

Kinetic energy
(v = velocity)

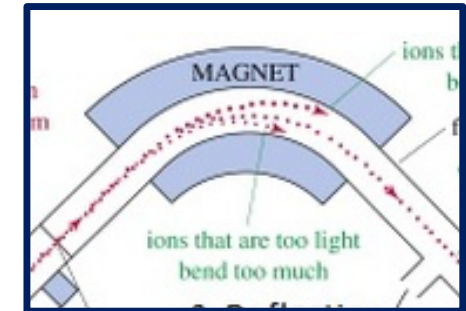
Potential energy



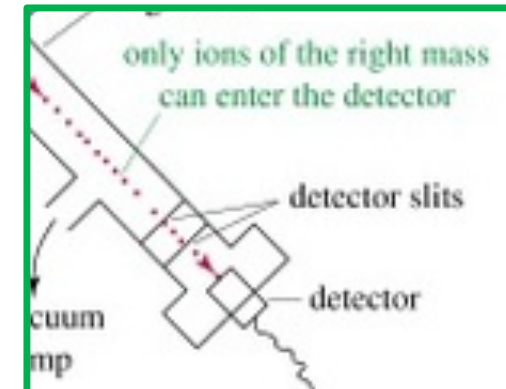
$$\frac{mv^2}{r} = zeVB \Rightarrow v = \frac{zeBr}{m}$$

Centripetal force

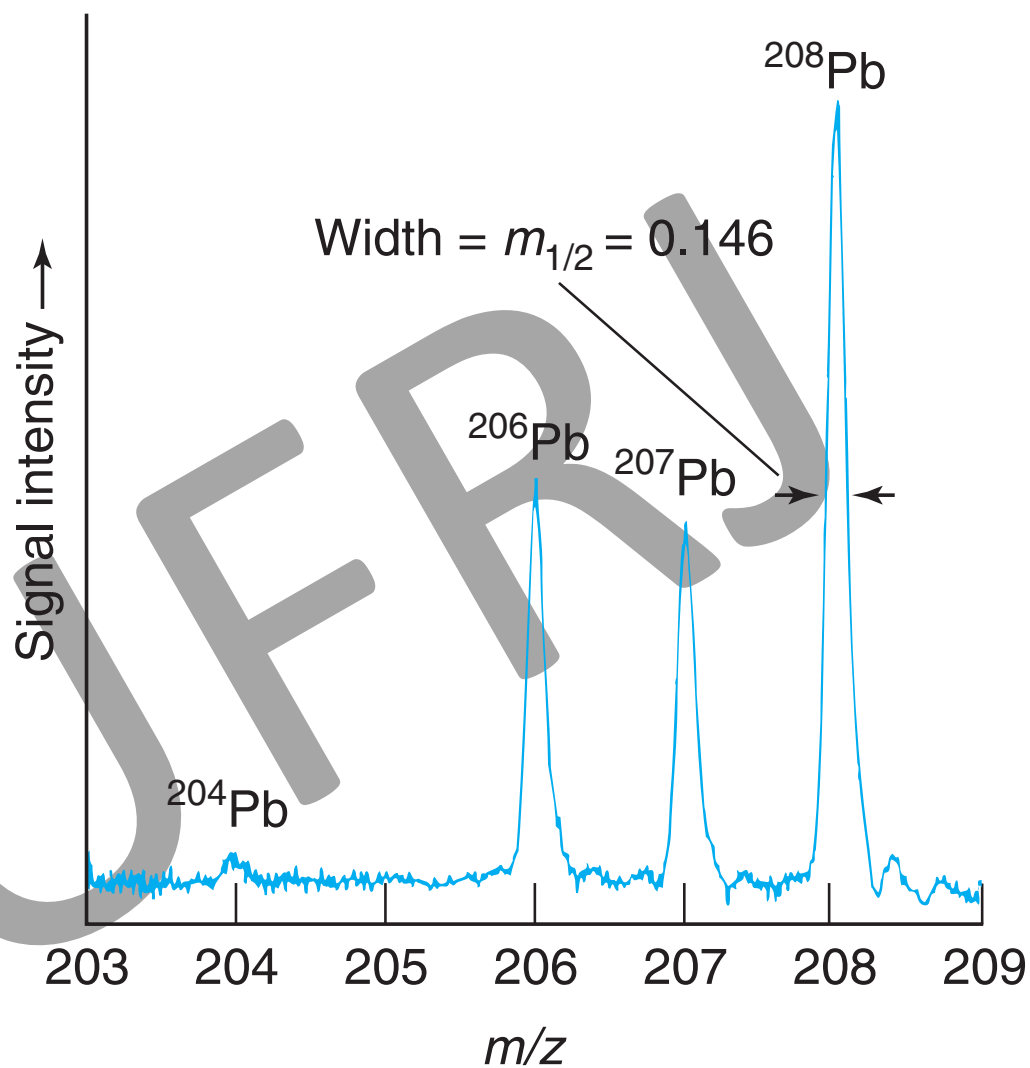
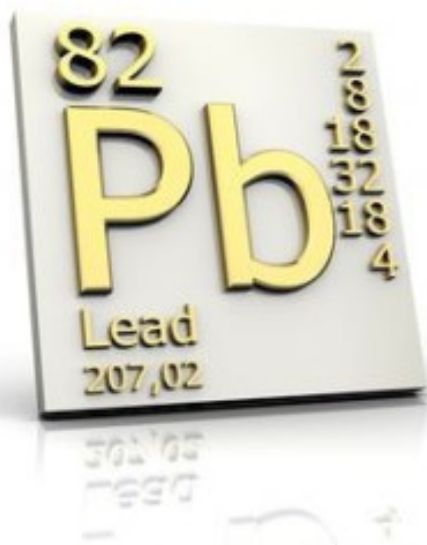
Magnetic force



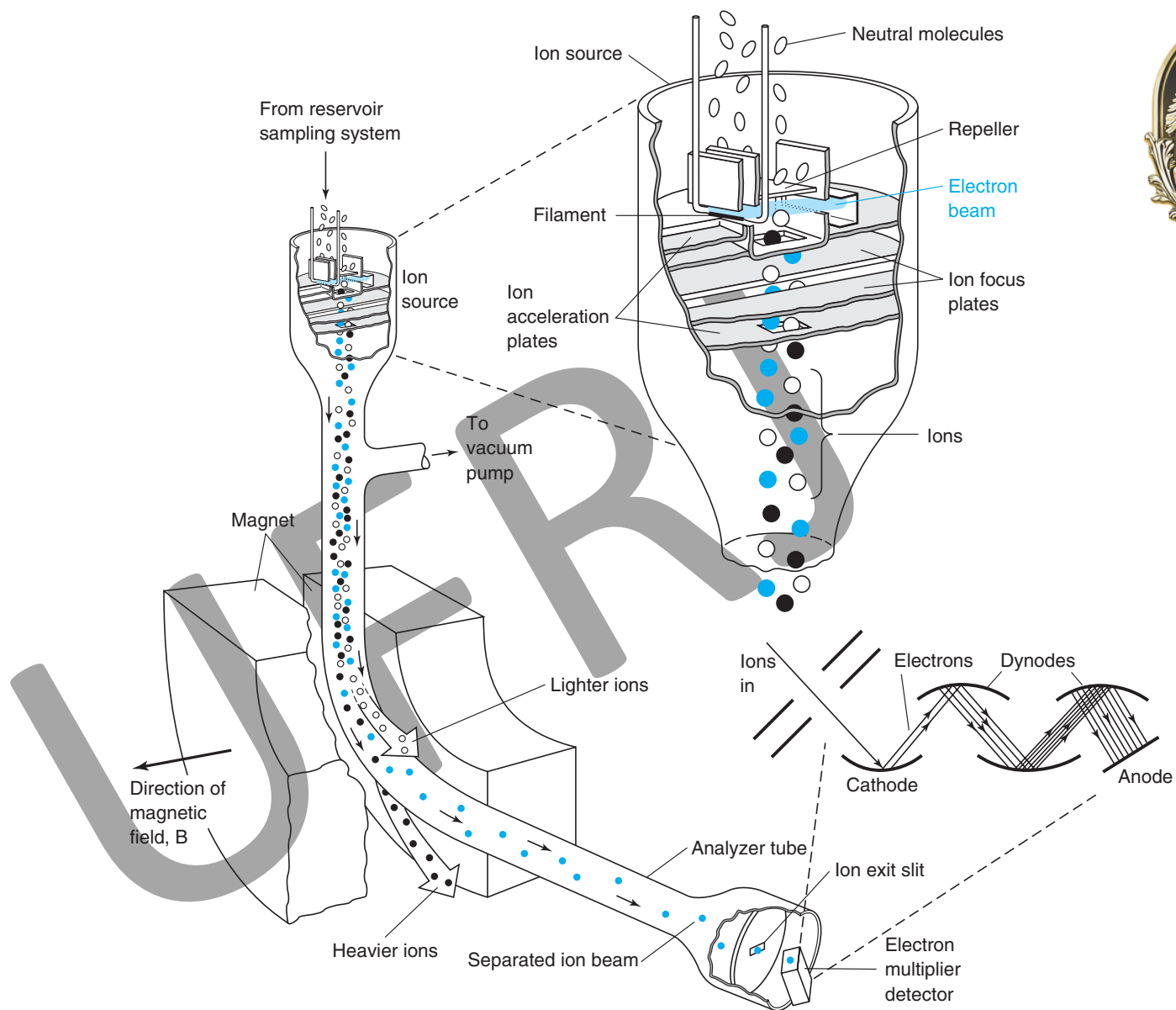
$$\frac{zeBr}{m} = \sqrt{\frac{2zeV}{m}} \Rightarrow \frac{m}{z} = \frac{eB^2r^2}{2V}$$



Espectro de Massas



Ionização eletrônica



Ionização



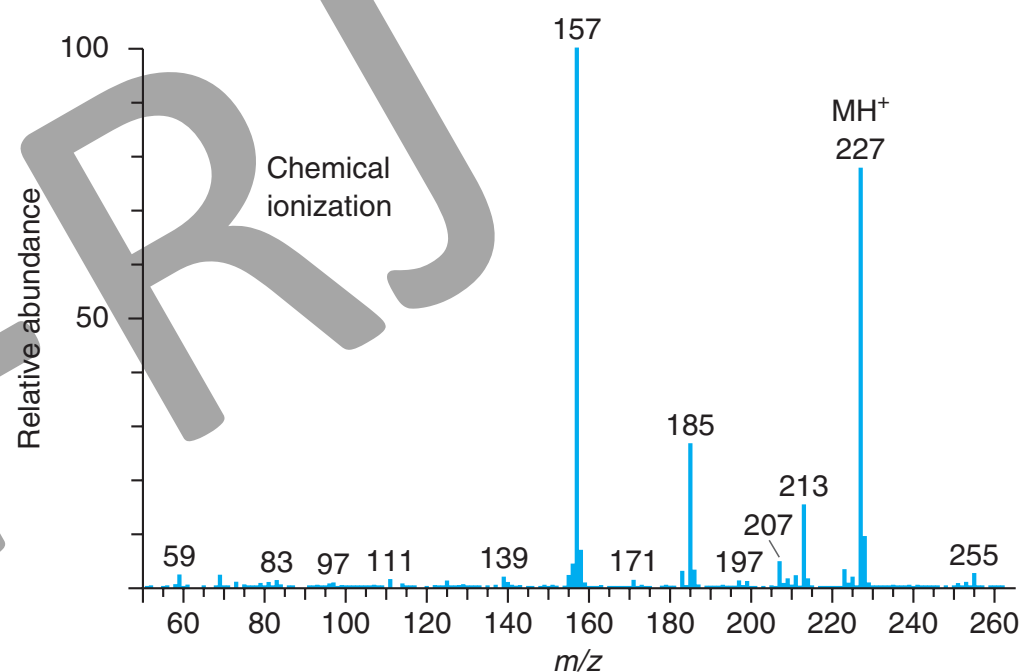
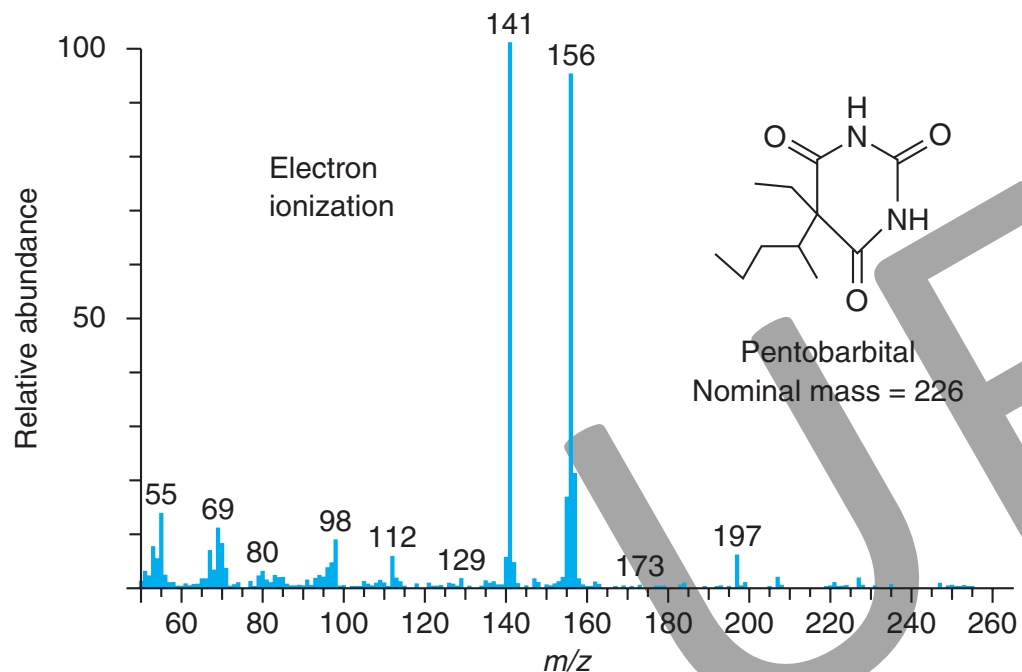
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Espectro de massas



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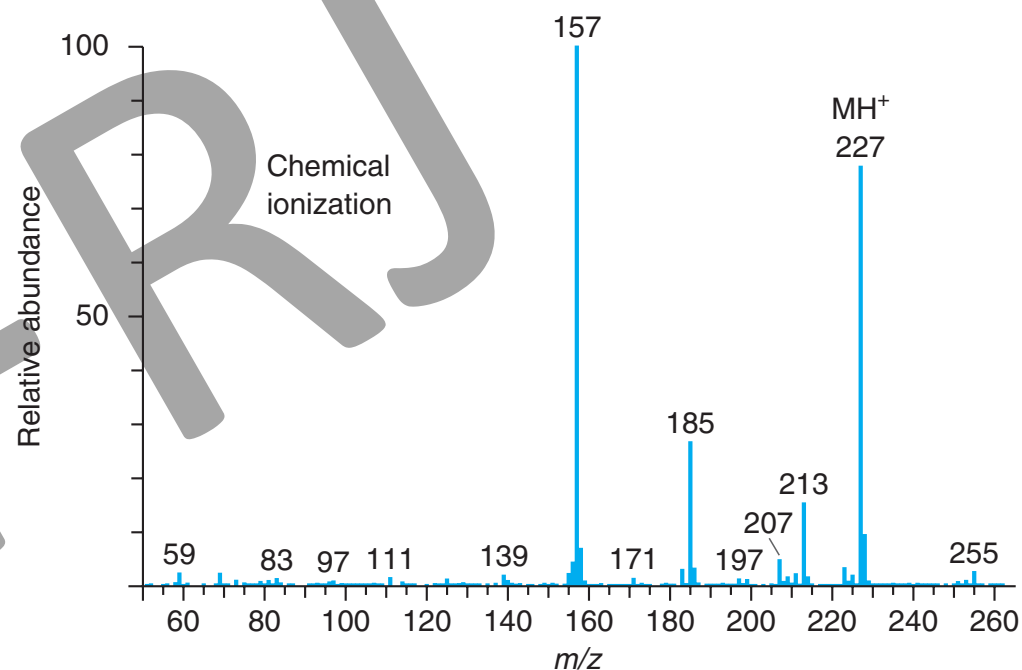
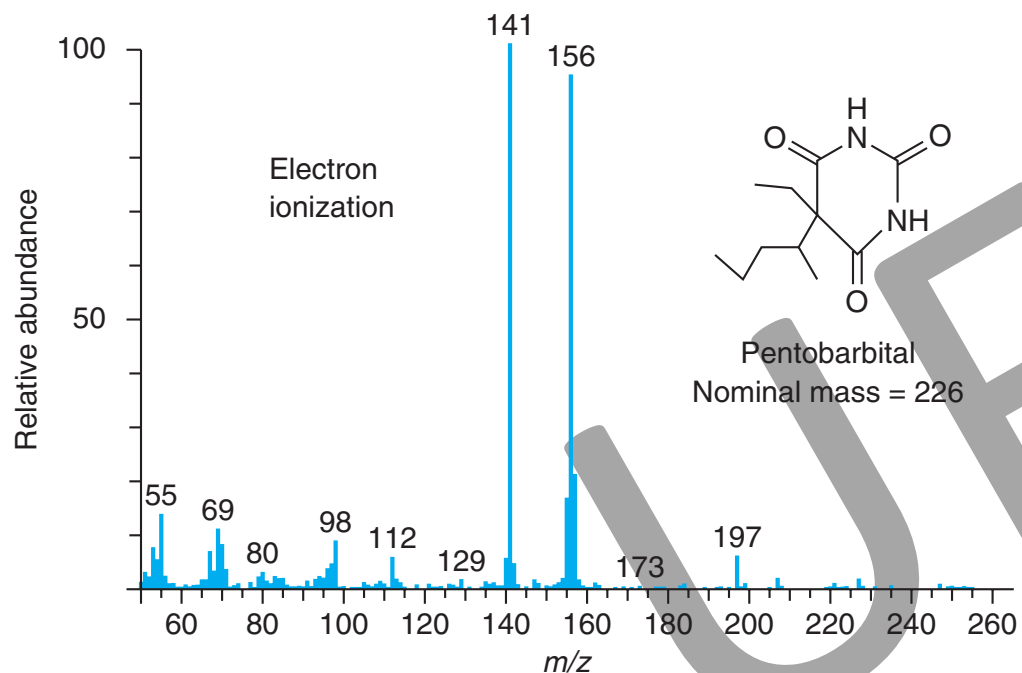
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Espectro de massas



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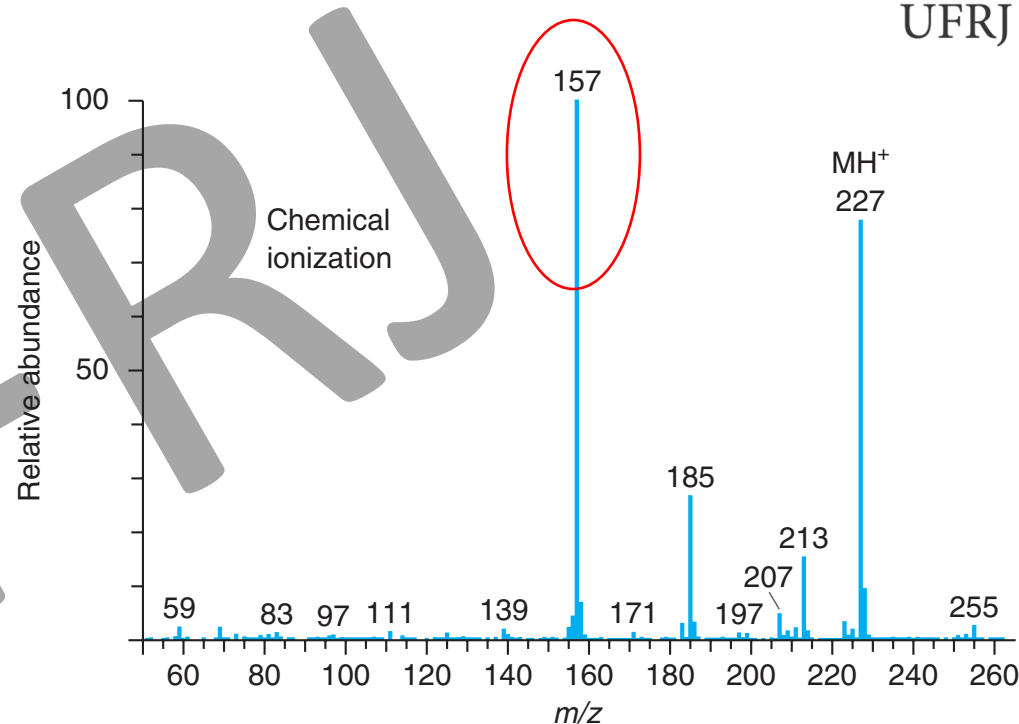
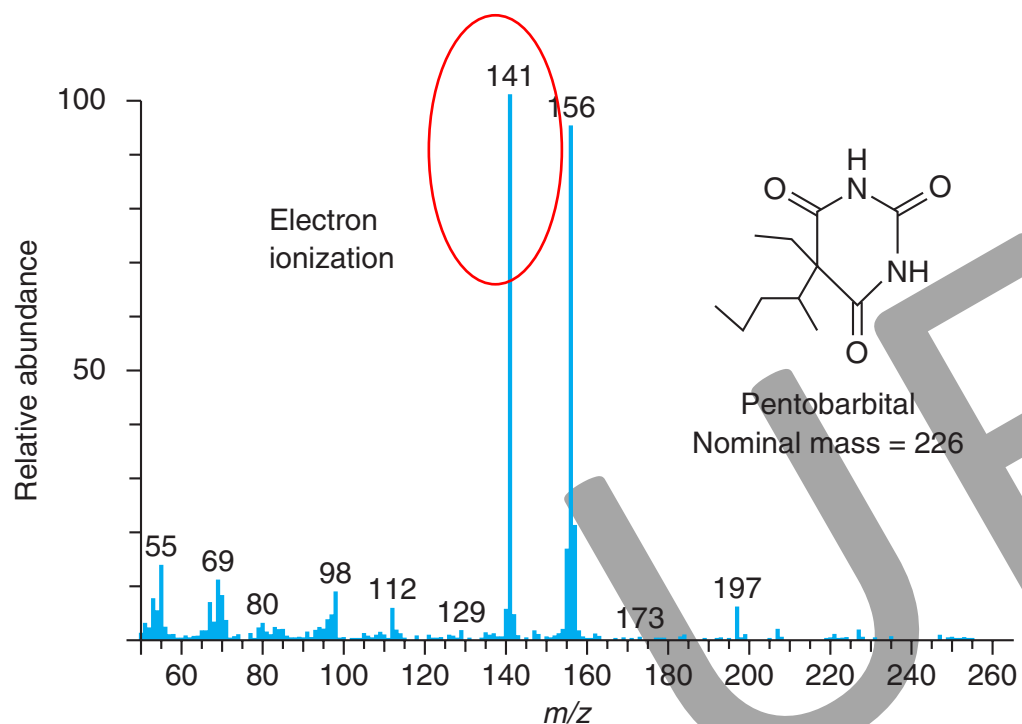
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Pico base

É o pico mais intenso do espectro



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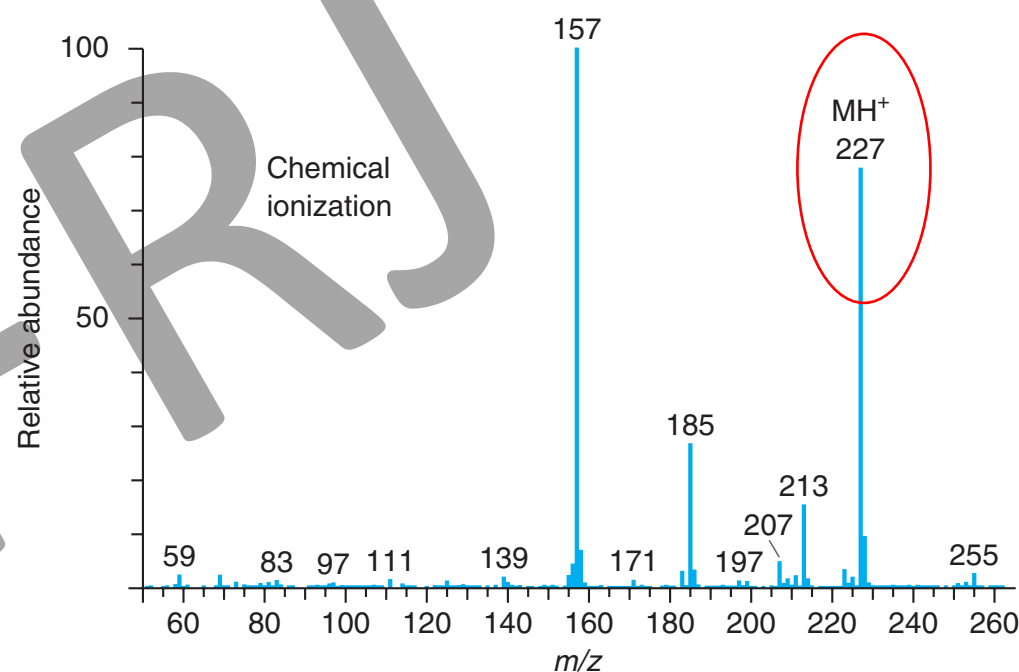
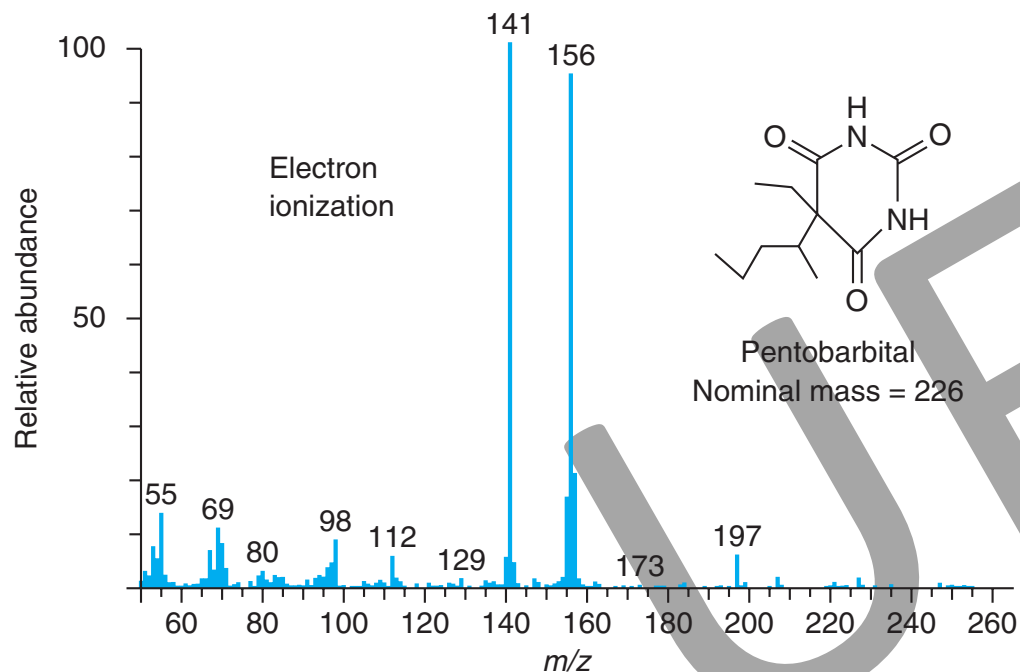
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Pico do íon molecular

É pequeno ou inexistente dependendo da molécula e do modo de ionização



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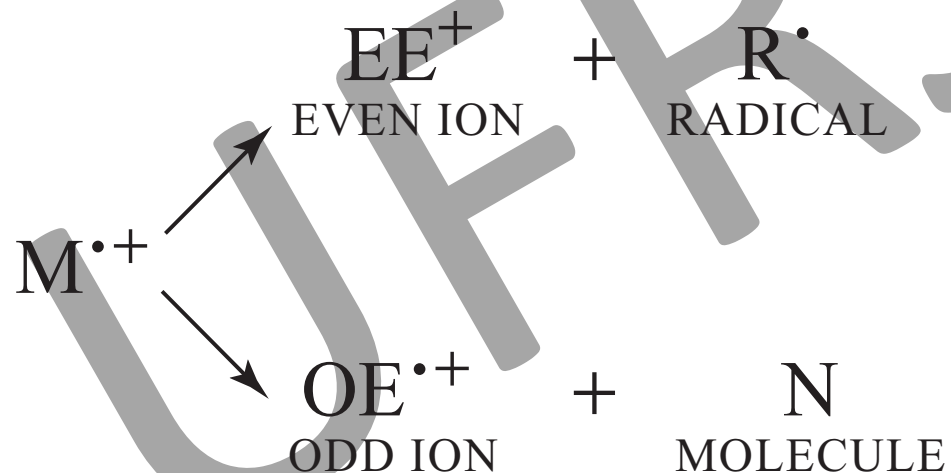
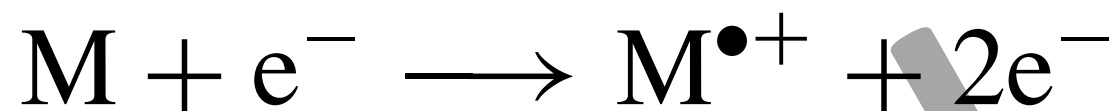
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Formação e íons

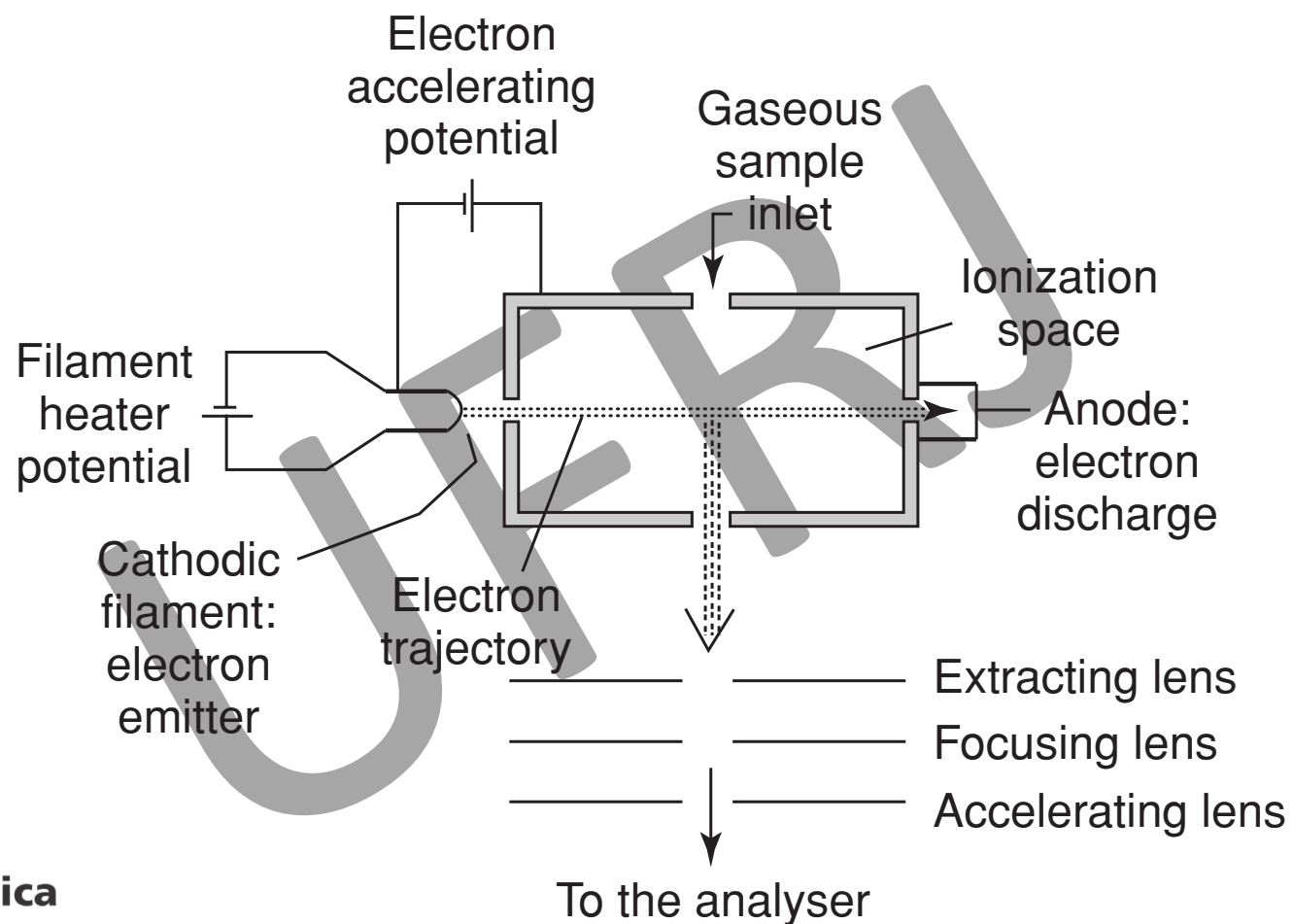


Ionização Eletrônica ou impacto eletrônico

70eV



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Ionização Eletrônica ou impacto eletrônico 70eV



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- Trabalha bem em moléculas em fase gasosa,
- Induz fragmentação extensiva na molécula
- Alta energia tende a fragmentar tudo

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Ionização Química



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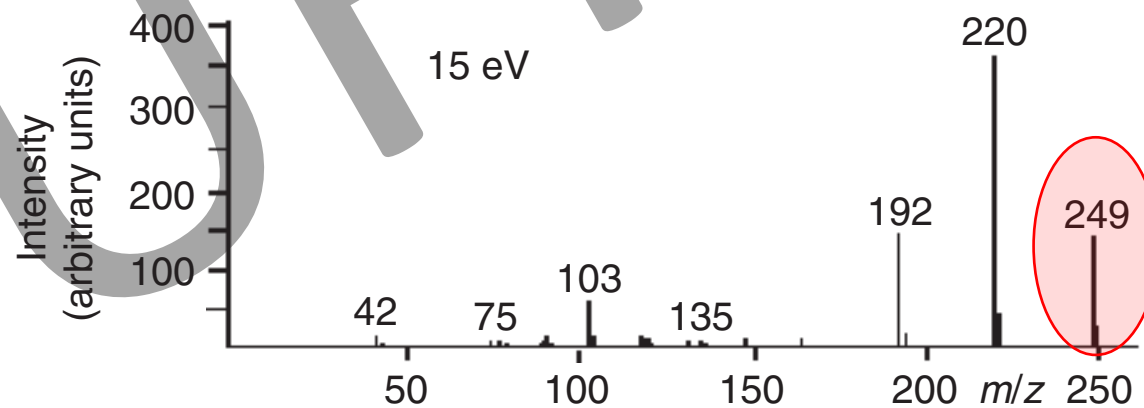
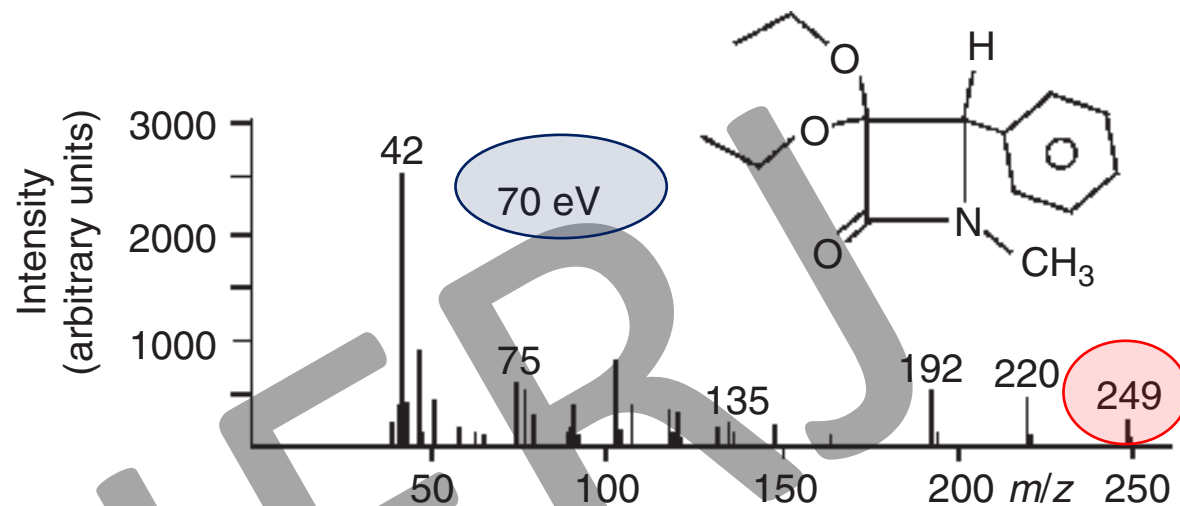
- Produz íons com pequeno excesso de energia
- Induz pouca fragmentação na molécula
- Espectro apresenta poucos fragmentos
- Técnica complementar à EI
- Gás contendo próton se choca com Molécula (M)
- Se a afinidade do Gás é menor que a afinidade da molécula temos MH^+ , $PA(G) < PA(M)$
- Gases comumente utilizados são Metano (5.7eV), isobutano(8,5eV) e amônia(9.0eV)



Ionização Química

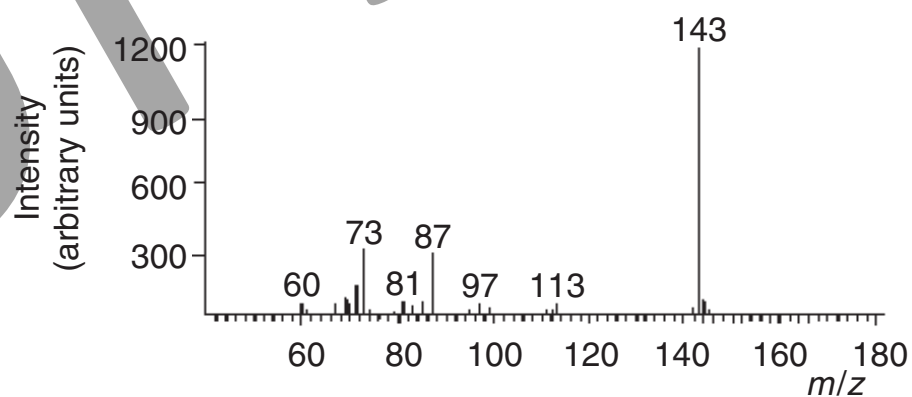
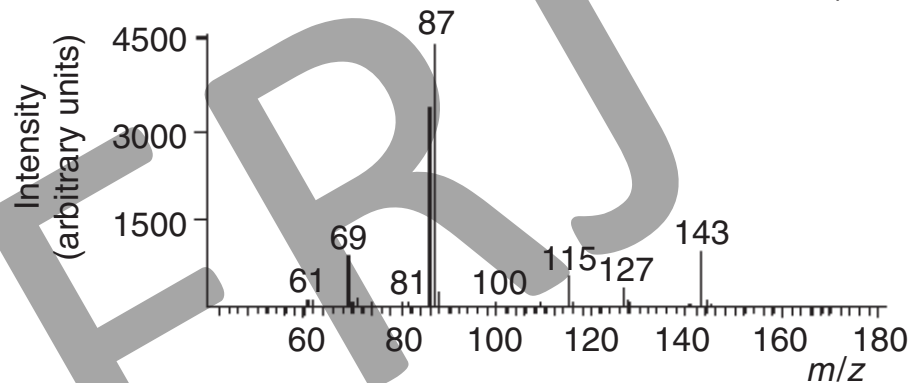
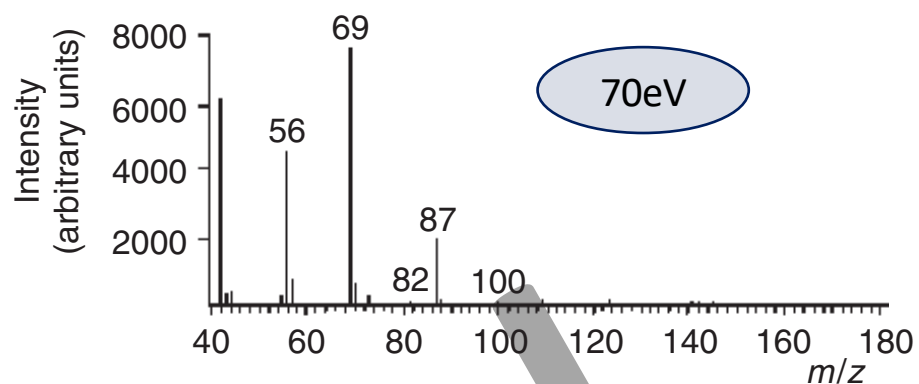
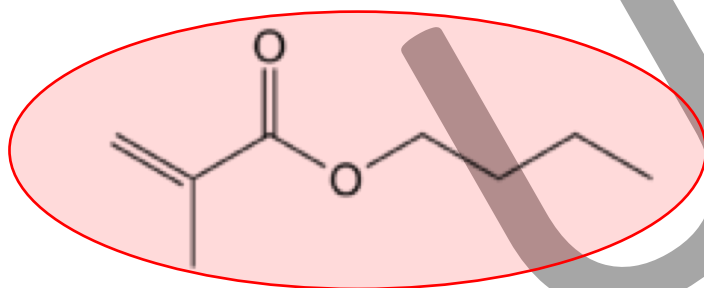
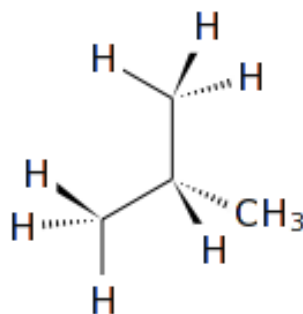


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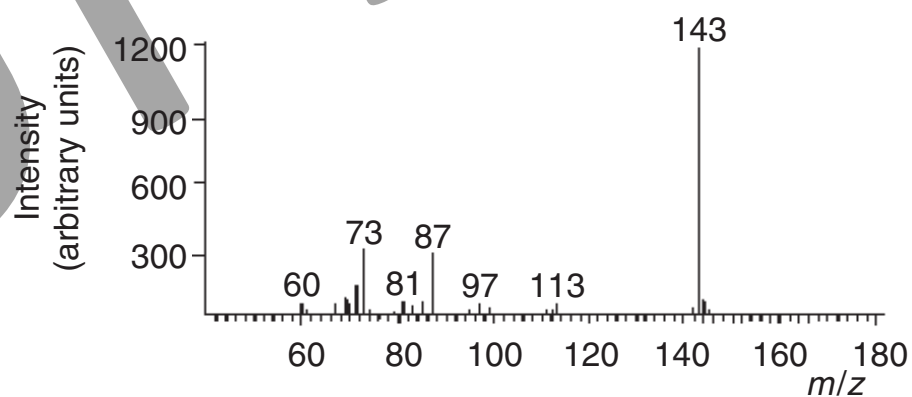
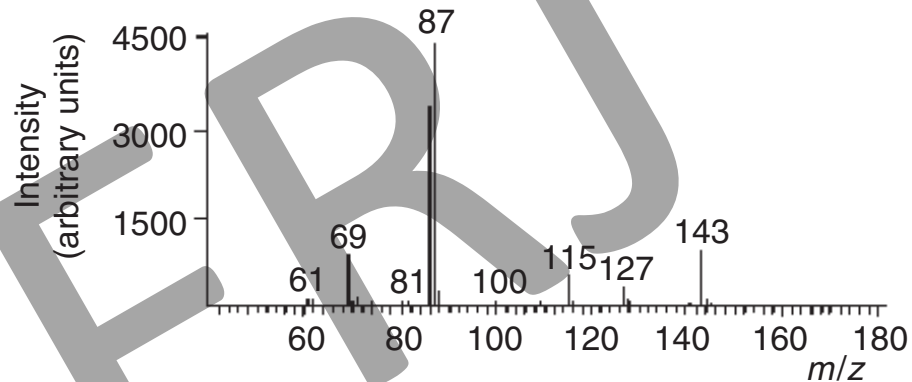
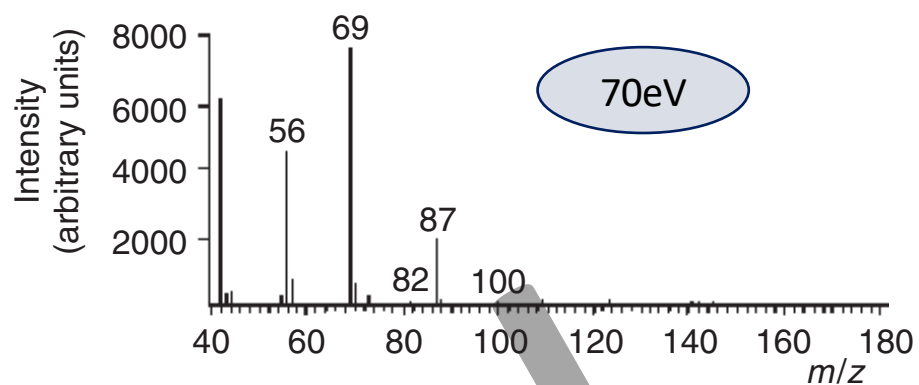
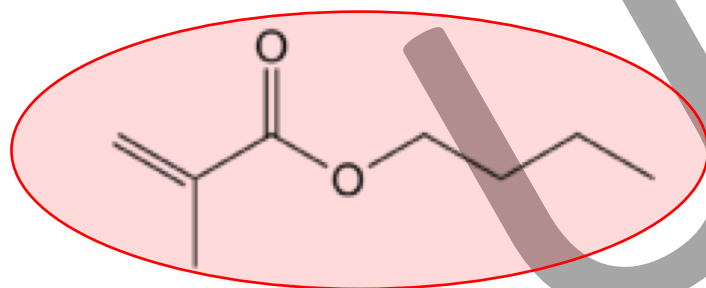
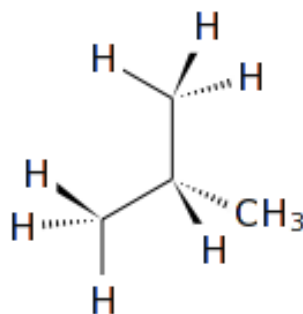


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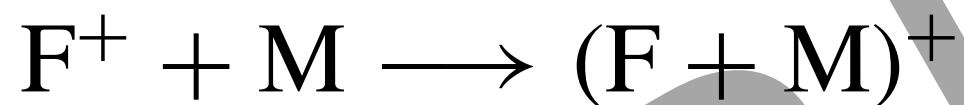
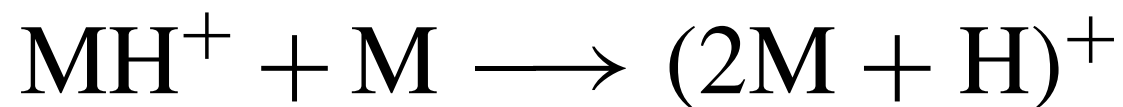
Ionização Química



Ionização Química



Formação de Adutos



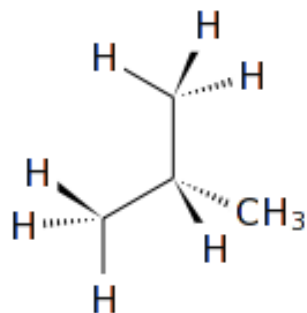
O plasma é responsável pela formação da associação de íons, também conhecidos como adutos



Formação de Adutos



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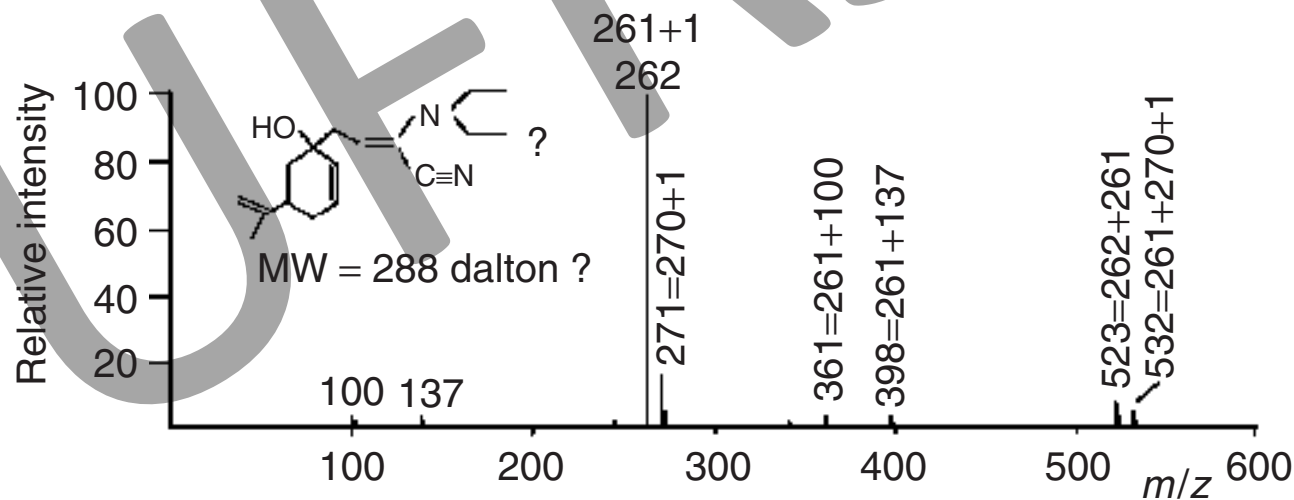
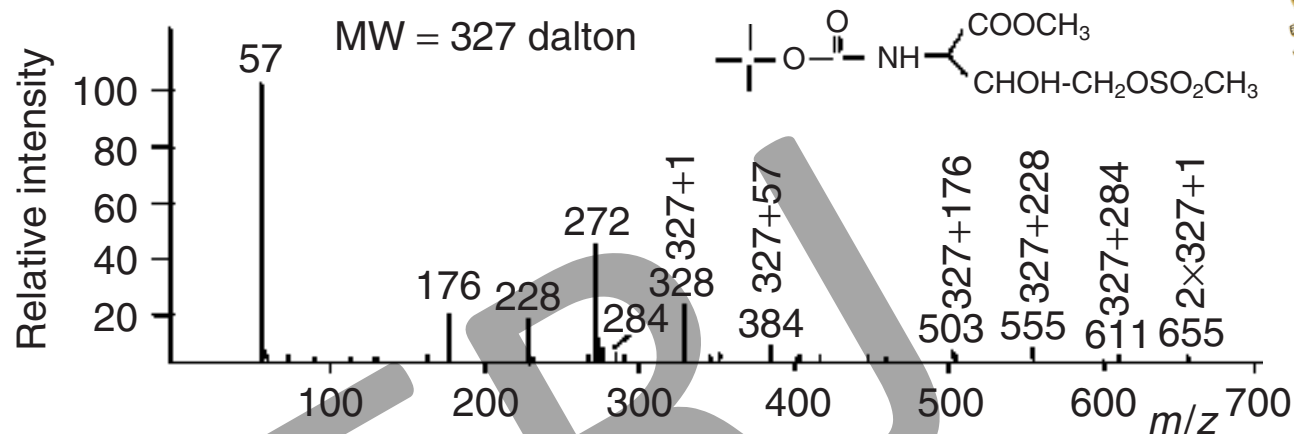


MW=58

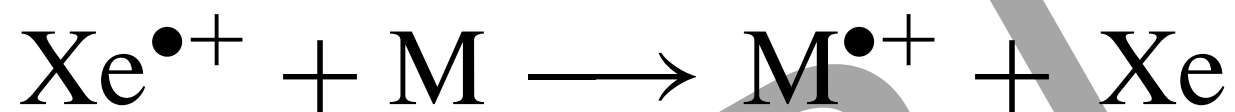
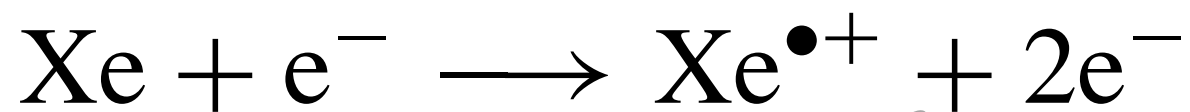
Mistura de
dois
compostos
261 e 270



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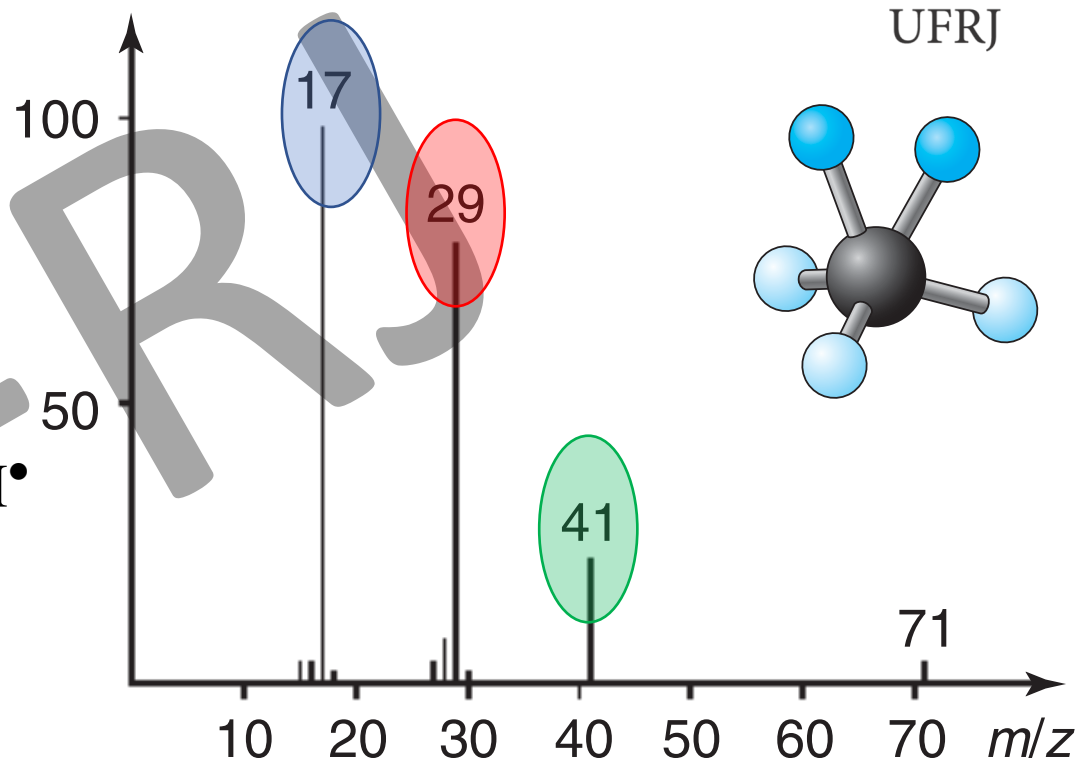
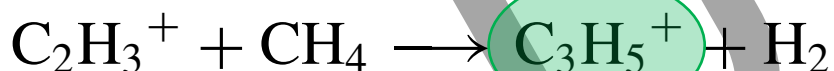
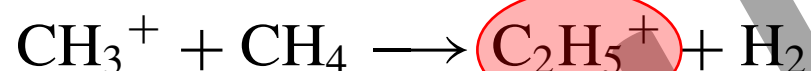
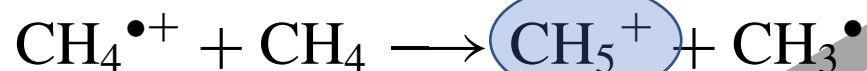
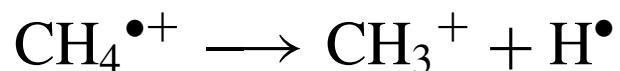
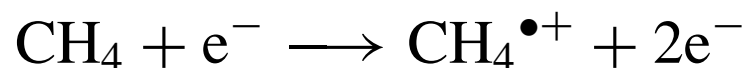
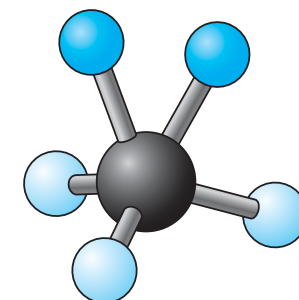
Transferência de carga



Ionização Química Metano



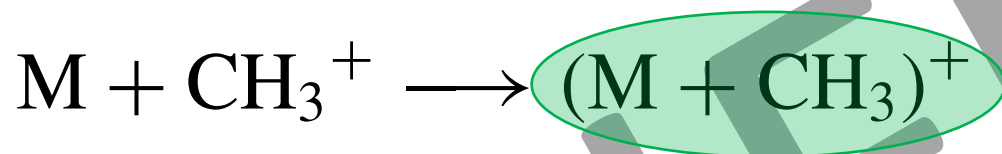
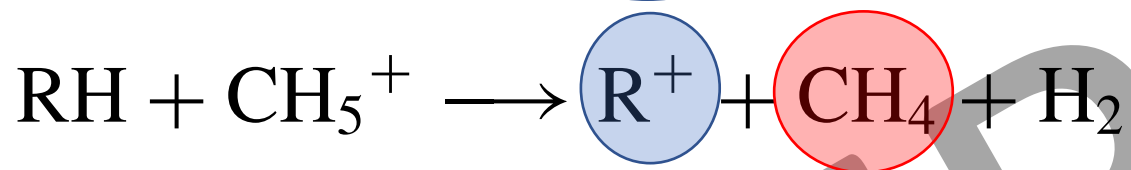
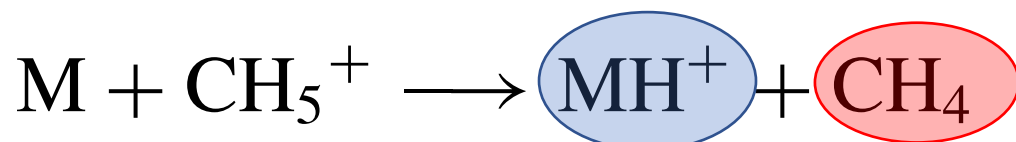
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Ionização Química



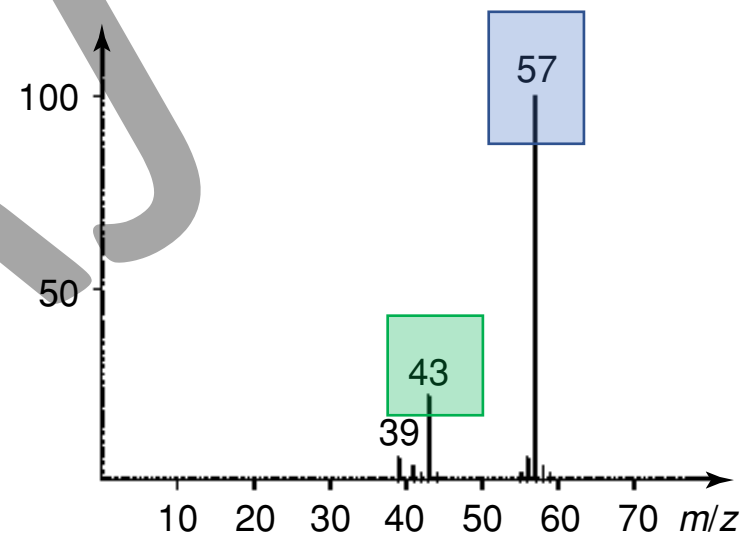
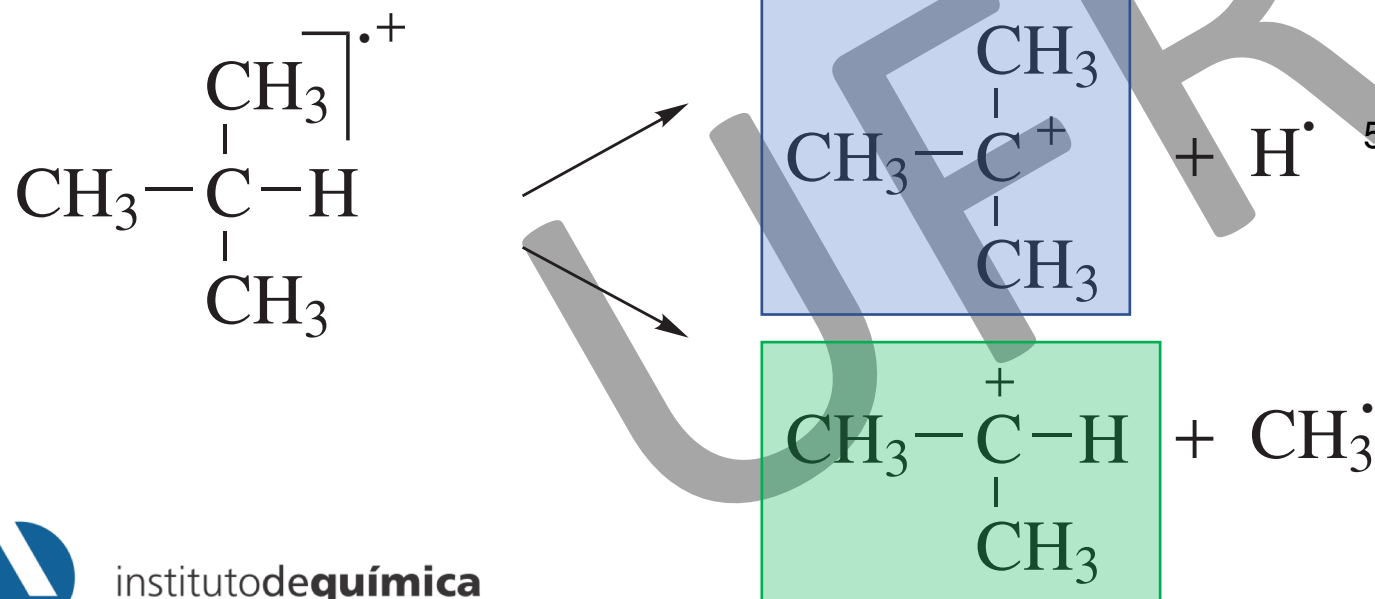
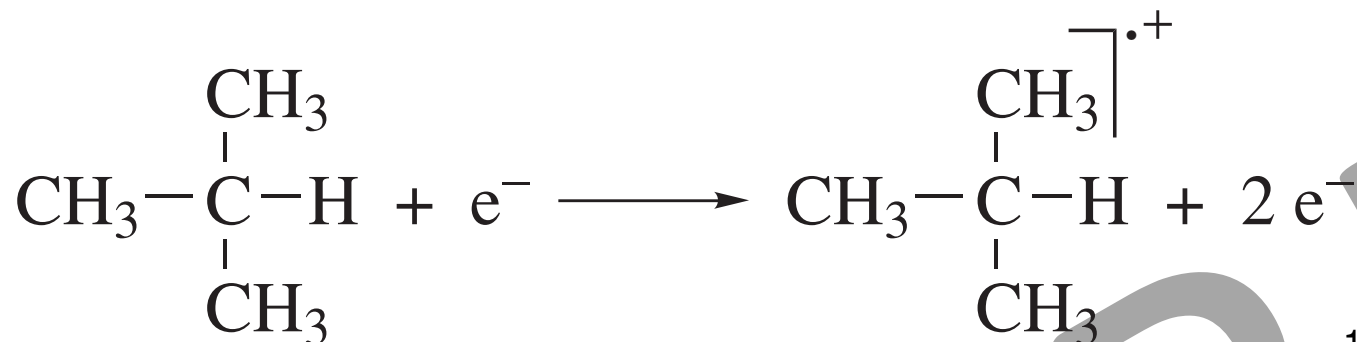
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Ionização Química Isobutano



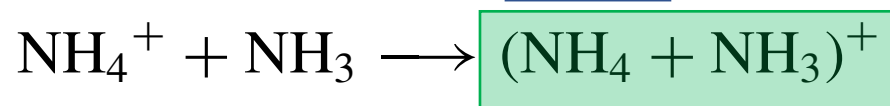
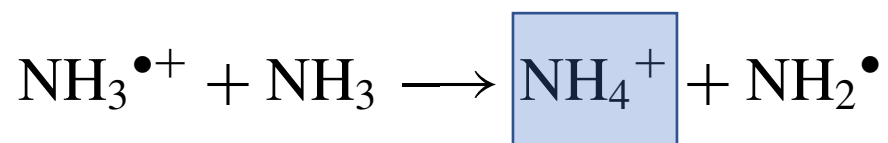
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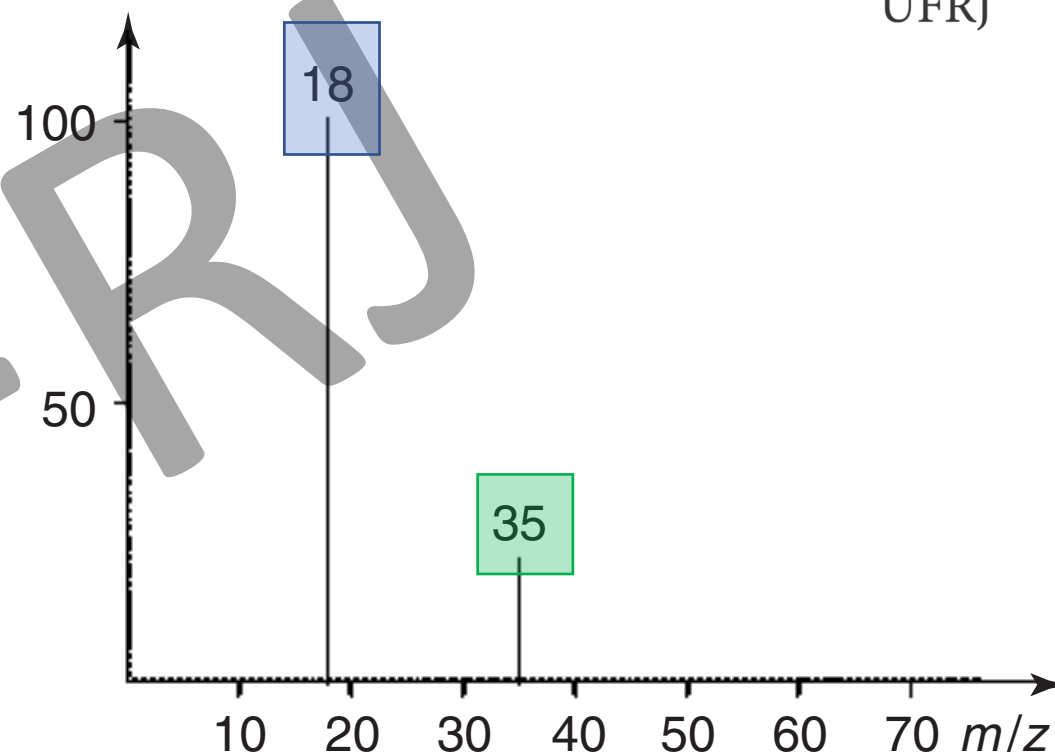


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Ionização Química Amônia



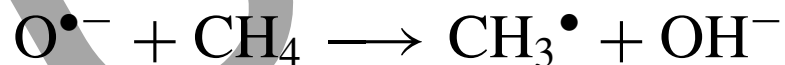
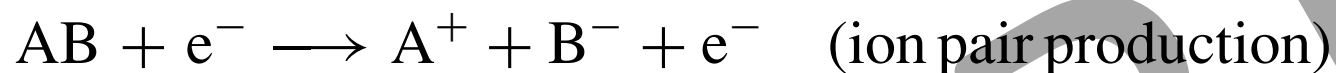
Generalizando



Formação de íons negativos



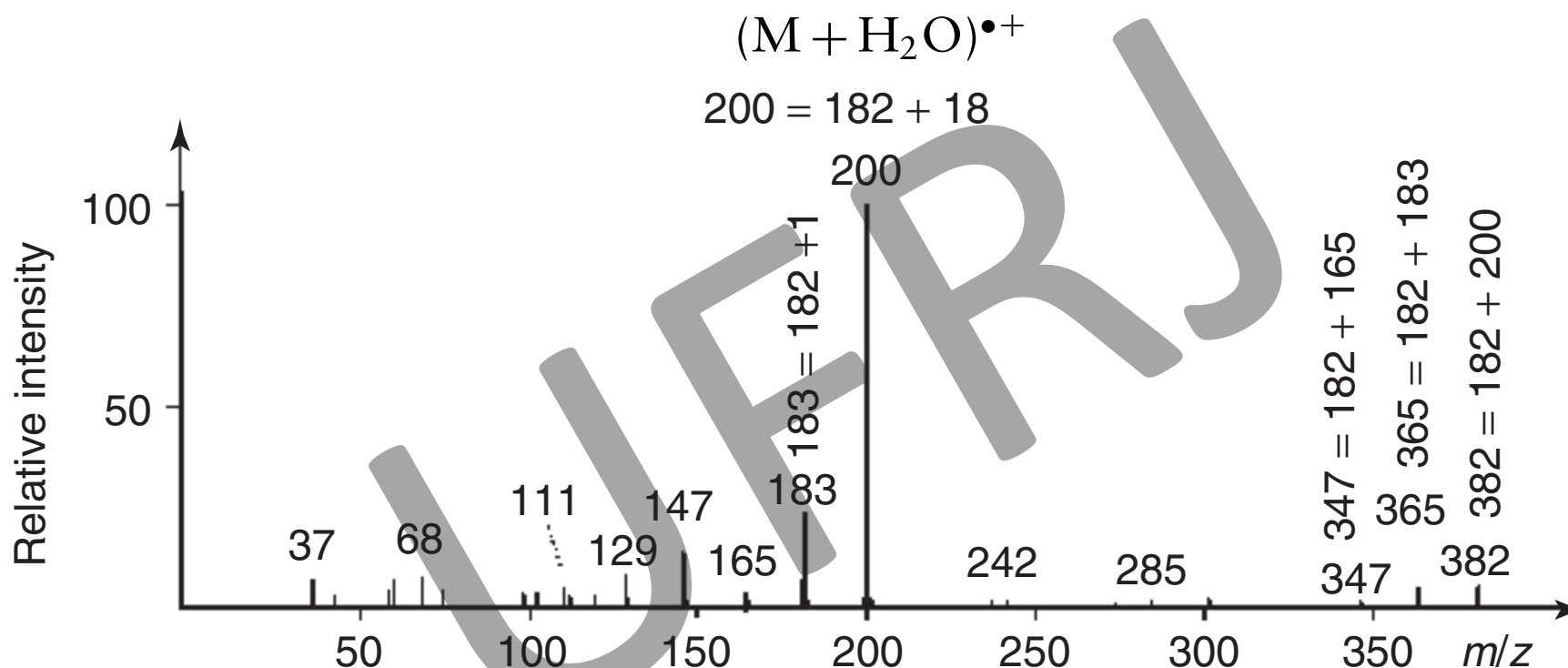
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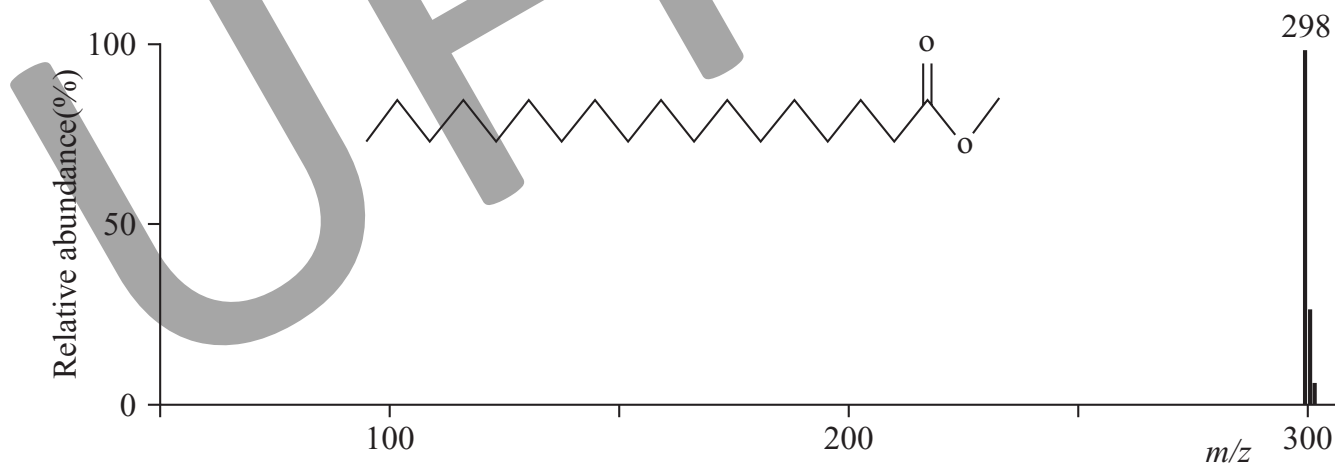
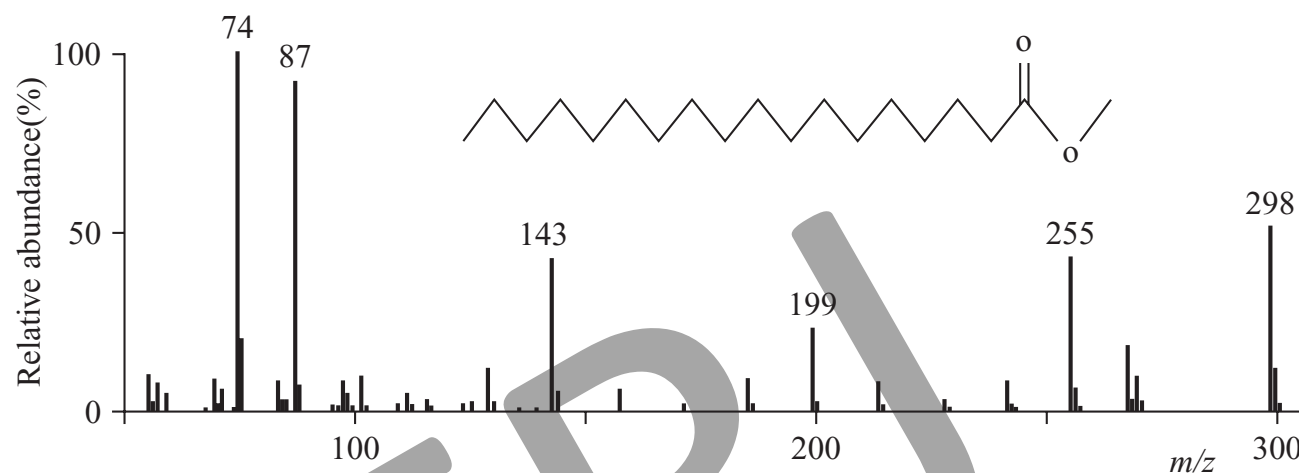
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Desorção ionização química



Field Ionization, Ionização por campo elétrico

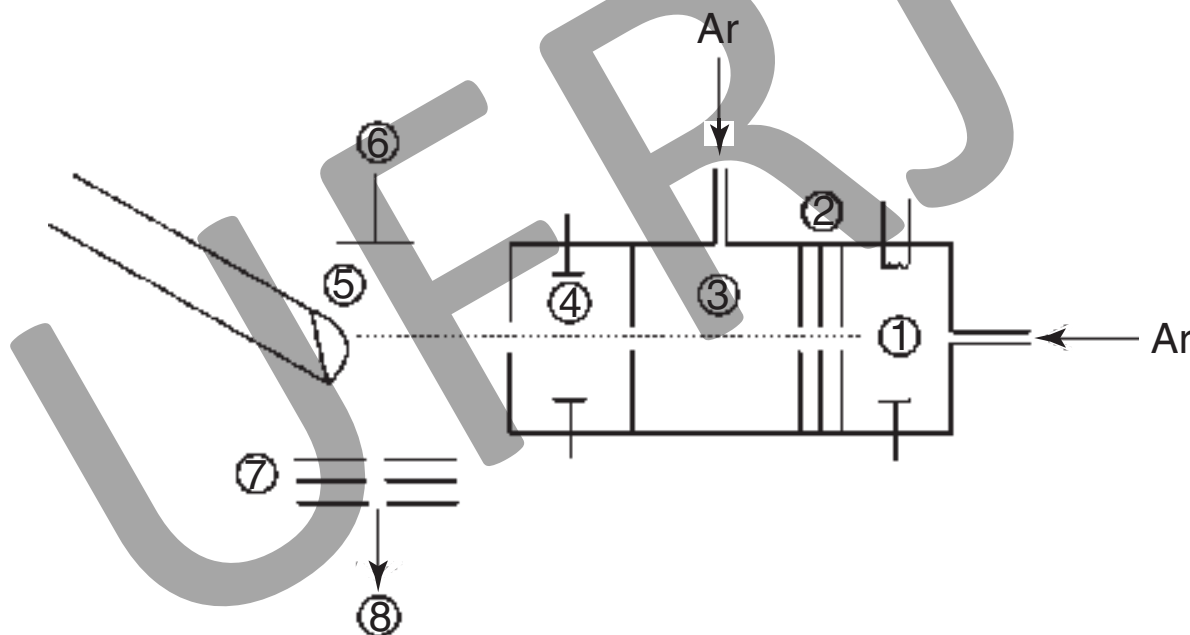
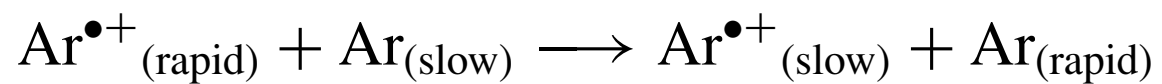
8-12kV





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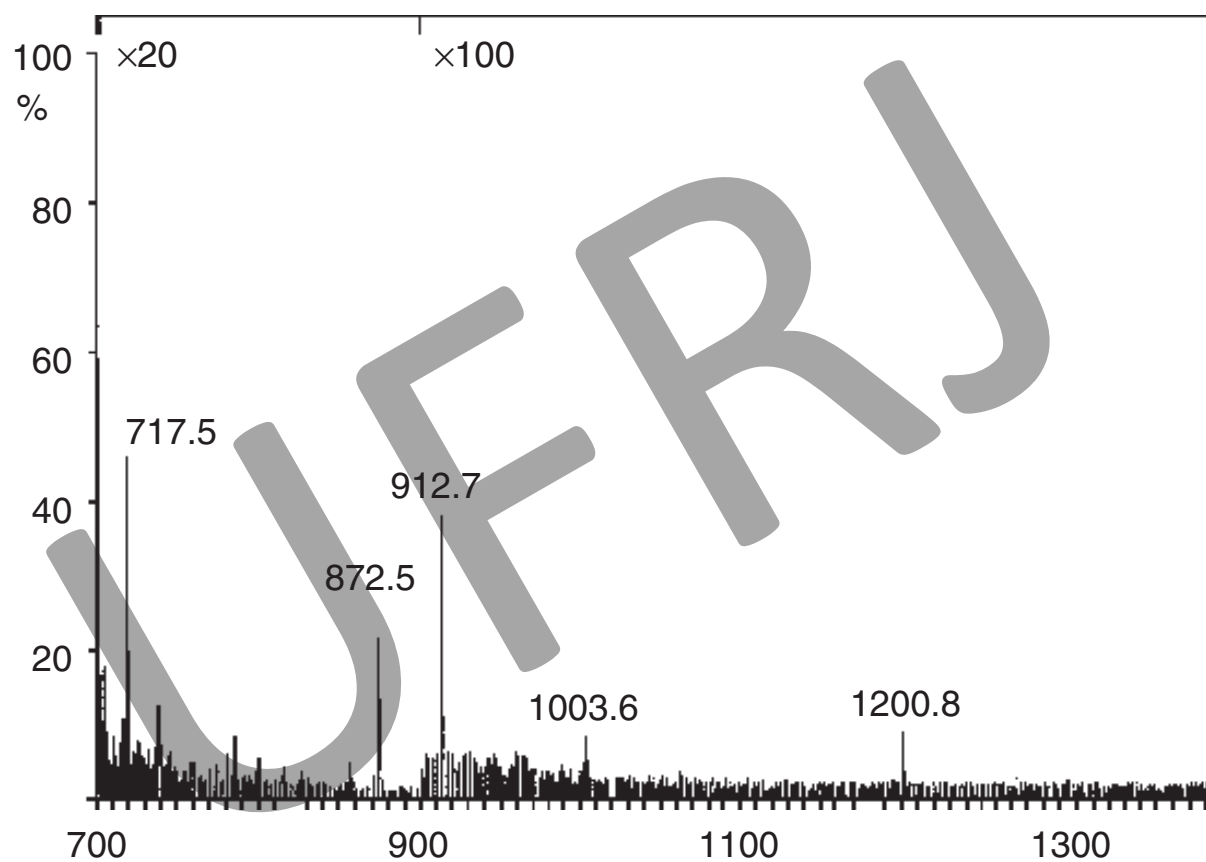
Fast Atom Bombardment - FAB



Fast Atom Bombardment - FAB



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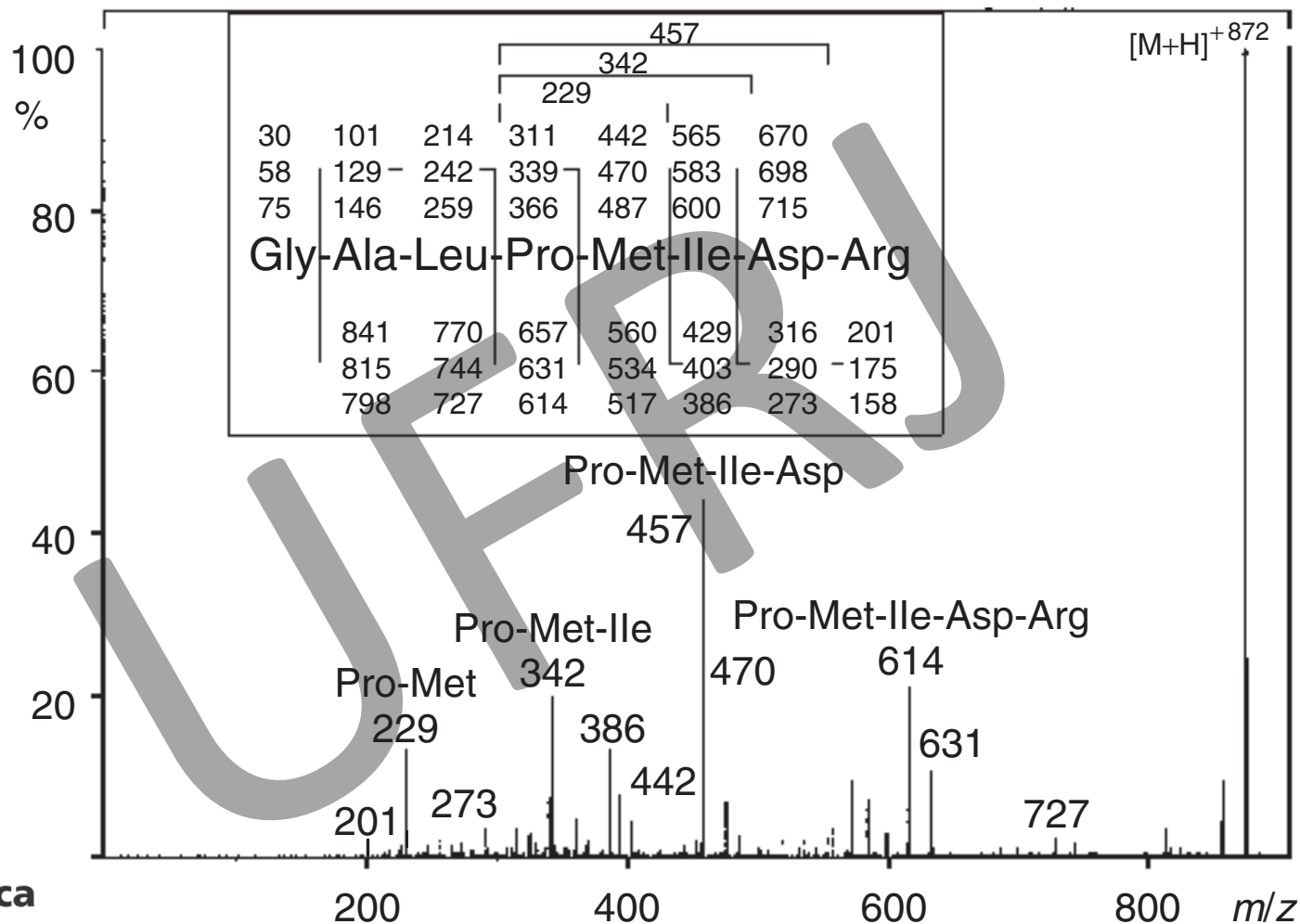
Fast Atom Bombardment - FAB

Secondary ion mass spectrometry (SIMS)



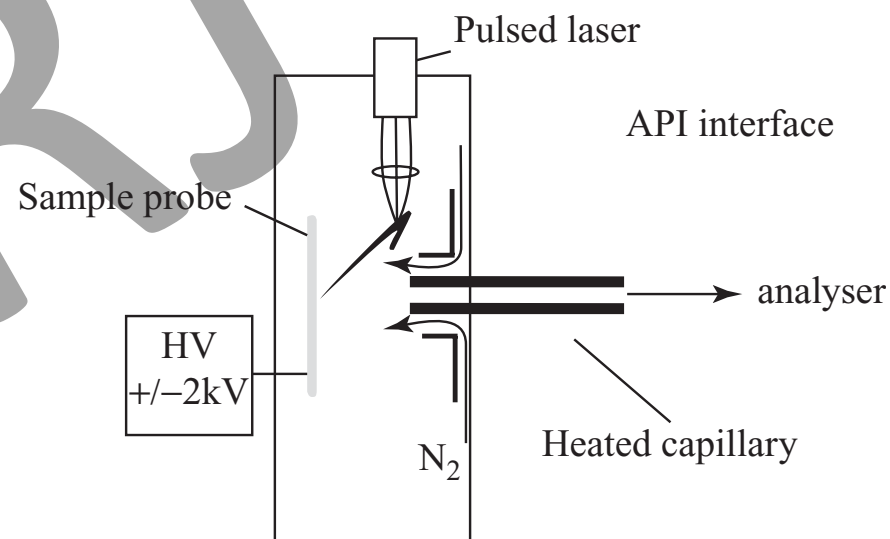
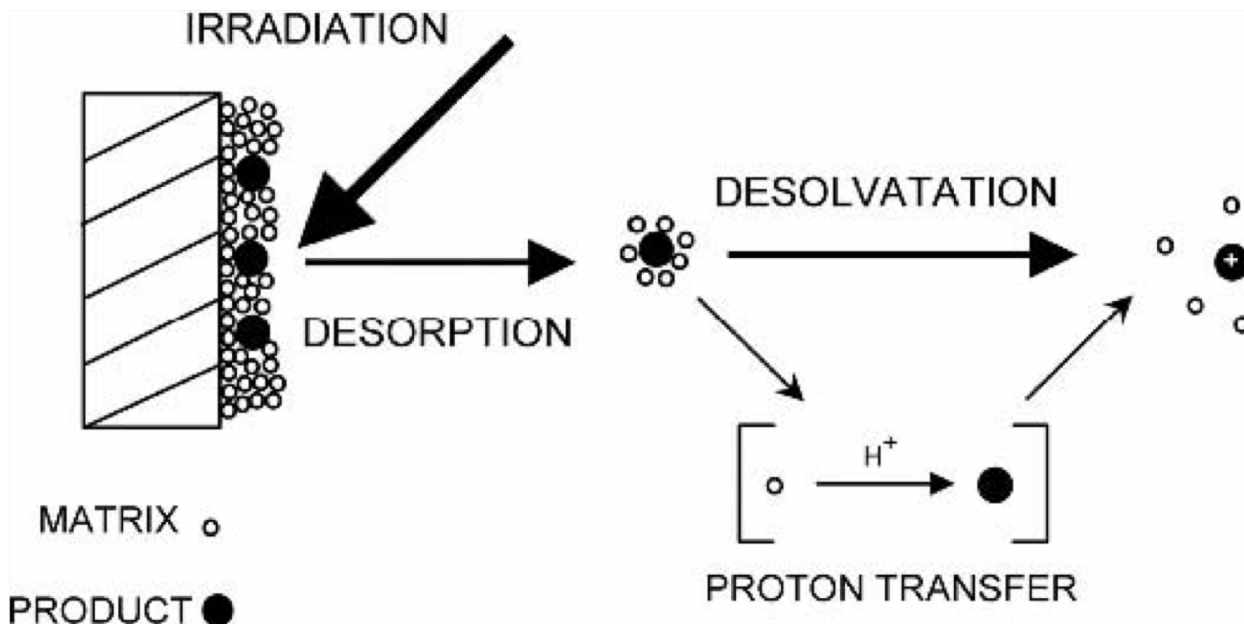
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SIMS = 872



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Matrix-Assisted Laser Desorption Ionization MALDI



Matrix-Assisted Laser Desorption Ionization **MALDI**



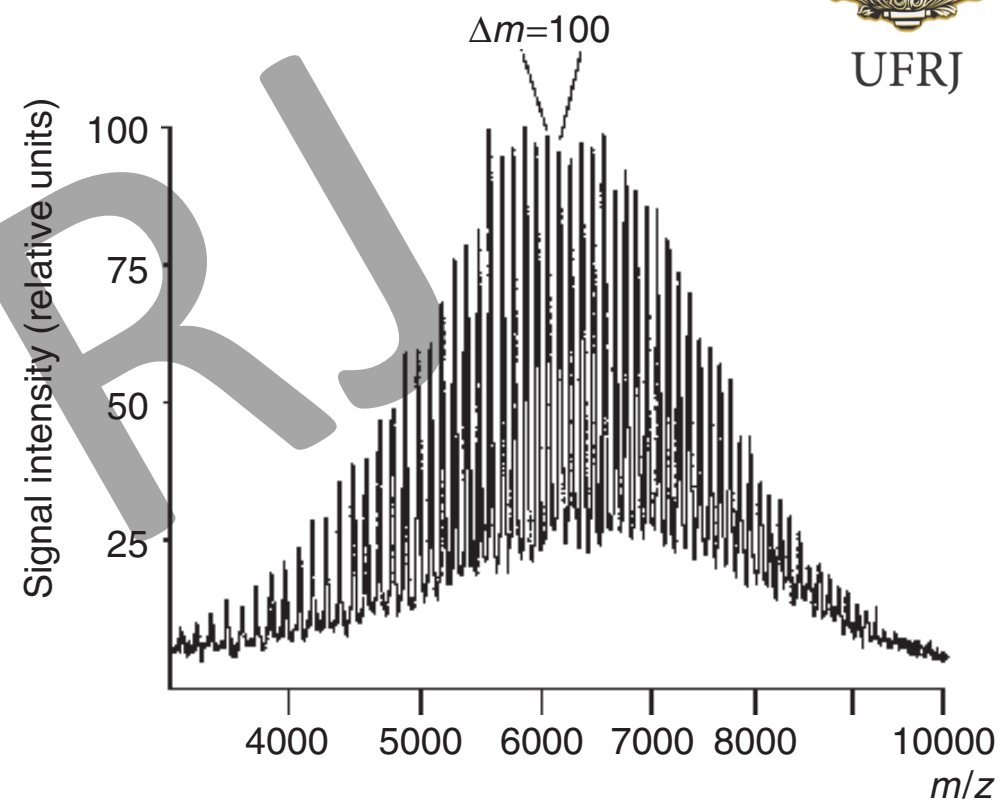
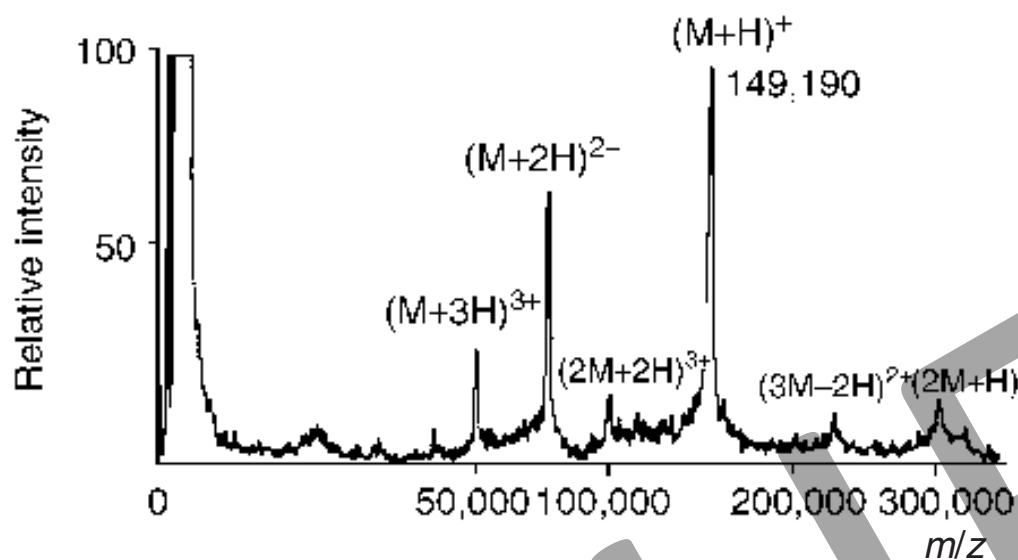
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Table 1.1 Some common lasers used for MALDI.

| Laser | Wavelength | Energy (eV) | Pulse width |
|-----------------|--------------------|-------------|-------------------------------|
| Nitrogen | 337 nm | 3.68 | <1 ns to a few ns |
| Nd:YAG $\mu 3$ | 355 nm | 3.49 | 5 ns |
| Nd:YAG $\mu 4$ | 266 nm | 4.66 | 5 ns |
| Er:YAG | 2.94 μm | 0.42 | 85 ns |
| CO ₂ | 10.6 μm | 0.12 | 100 ns + 1 μs tail |



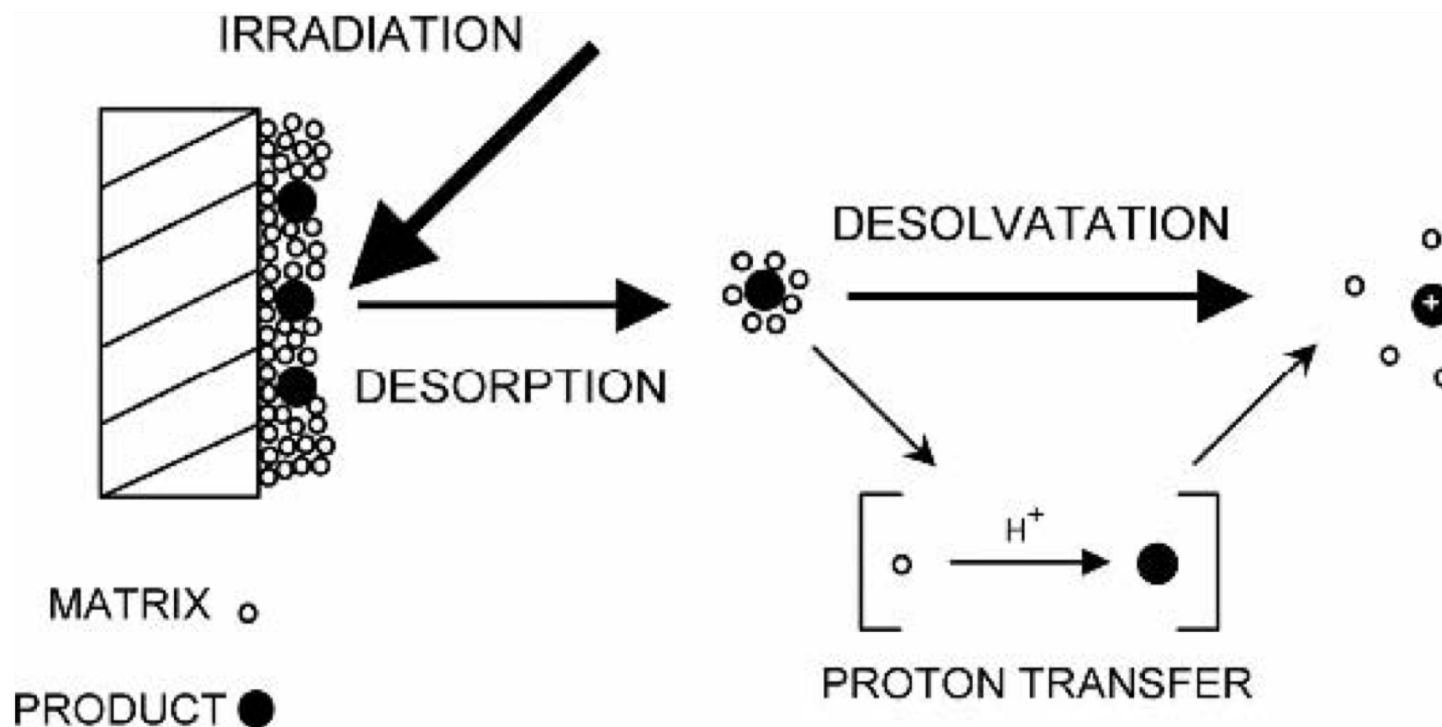
Matrix-Assisted Laser Desorption Ionization MALDI



Matrix-Assisted Laser Desorption Ionization MALDI



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Matrix-Assisted Laser Desorption Ionization MALDI



Table 1.2 Some common UV-MALDI matrices.

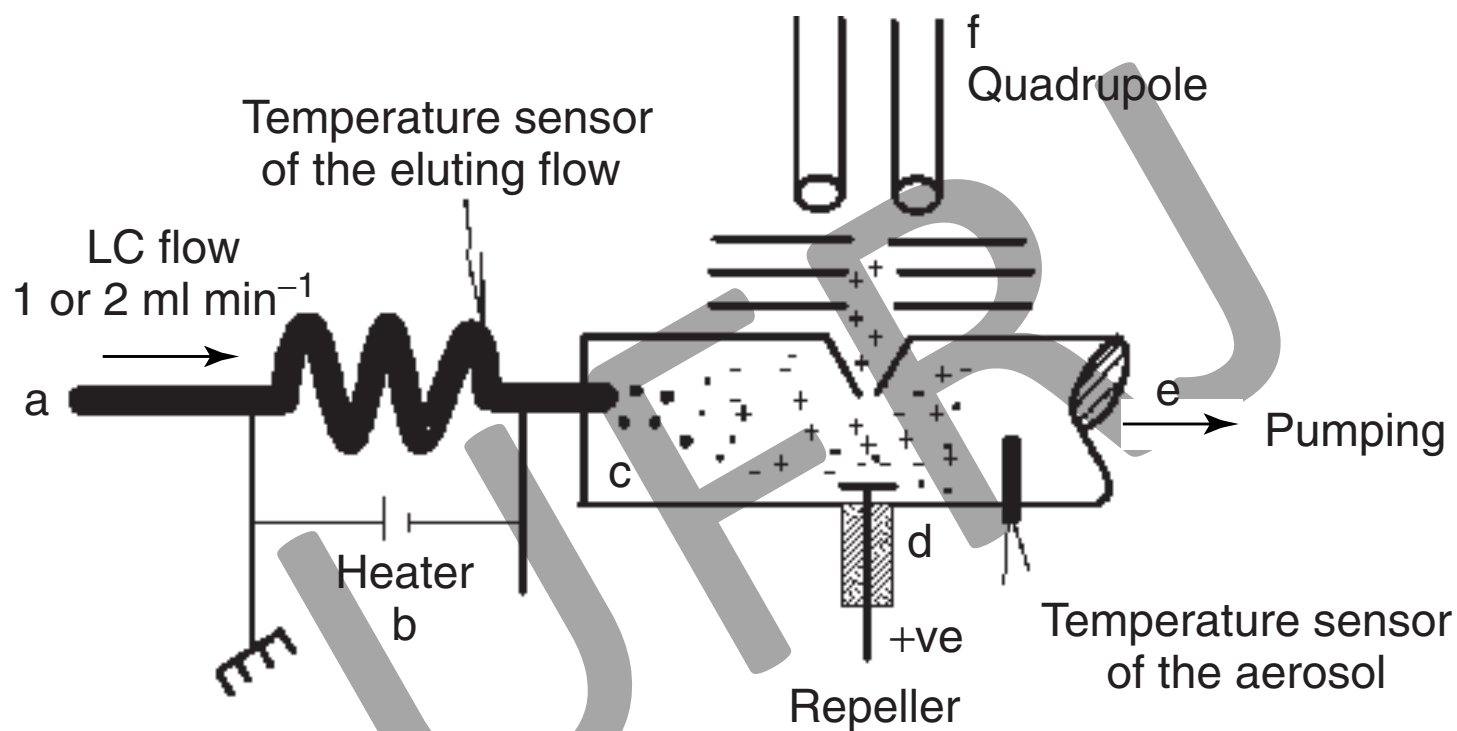
| Analyte | Matrix | Abbreviation |
|---------------------|--|--------------|
| Peptides/proteins | α -Cyano-4-hydroxycinnamic acid | CHCA |
| | 2,5-Dihydroxybenzoic acid (gentisic) | DHB |
| | 3,5-Dimethoxy-4-hydroxycinnamic acid (sinapic) | SA |
| Oligonucleotides | Trihydroxyacetophenone | THAP |
| | 3-Hydroxypicolinic acid | HPA |
| Carbohydrates | 2,5-Dihydroxybenzoic acid | DHB |
| | α -Cyano-4-hydroxycinnamic acid | CHCA |
| | Trihydroxyacetophenone | THAP |
| Synthetic polymers | Trans-3-indoleacrylic acid | IAA |
| | Dithranol | DIT |
| | 2,5-Dihydroxybenzoic acid | DHB |
| Organic molecules | 2,5-Dihydroxybenzoic acid | DHB |
| Inorganic molecules | Trans-2-(3-(4-tert-Butylphenyl)-2methyl-2-propenyliedene)malononitrile | DCTB |
| Lipids | Dithranol | DIT |



Termo spray



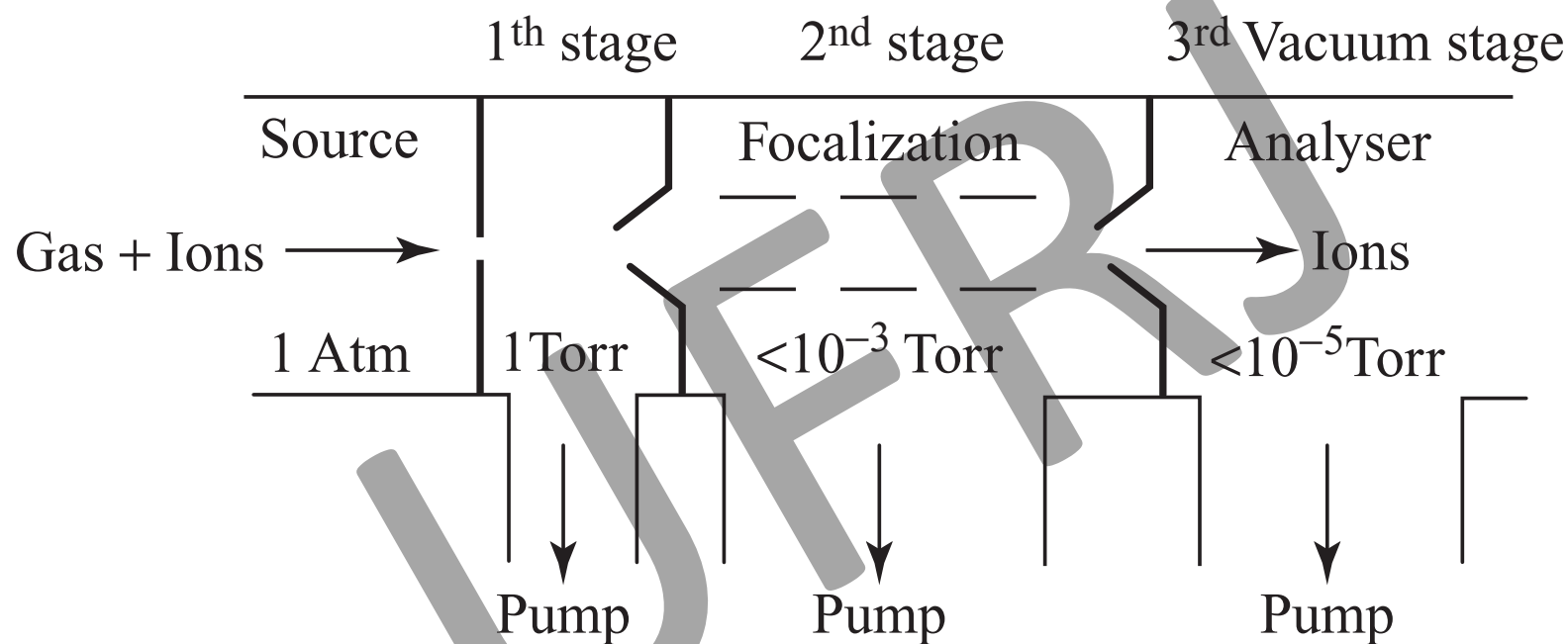
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API – Ionização a pressão atmosférica



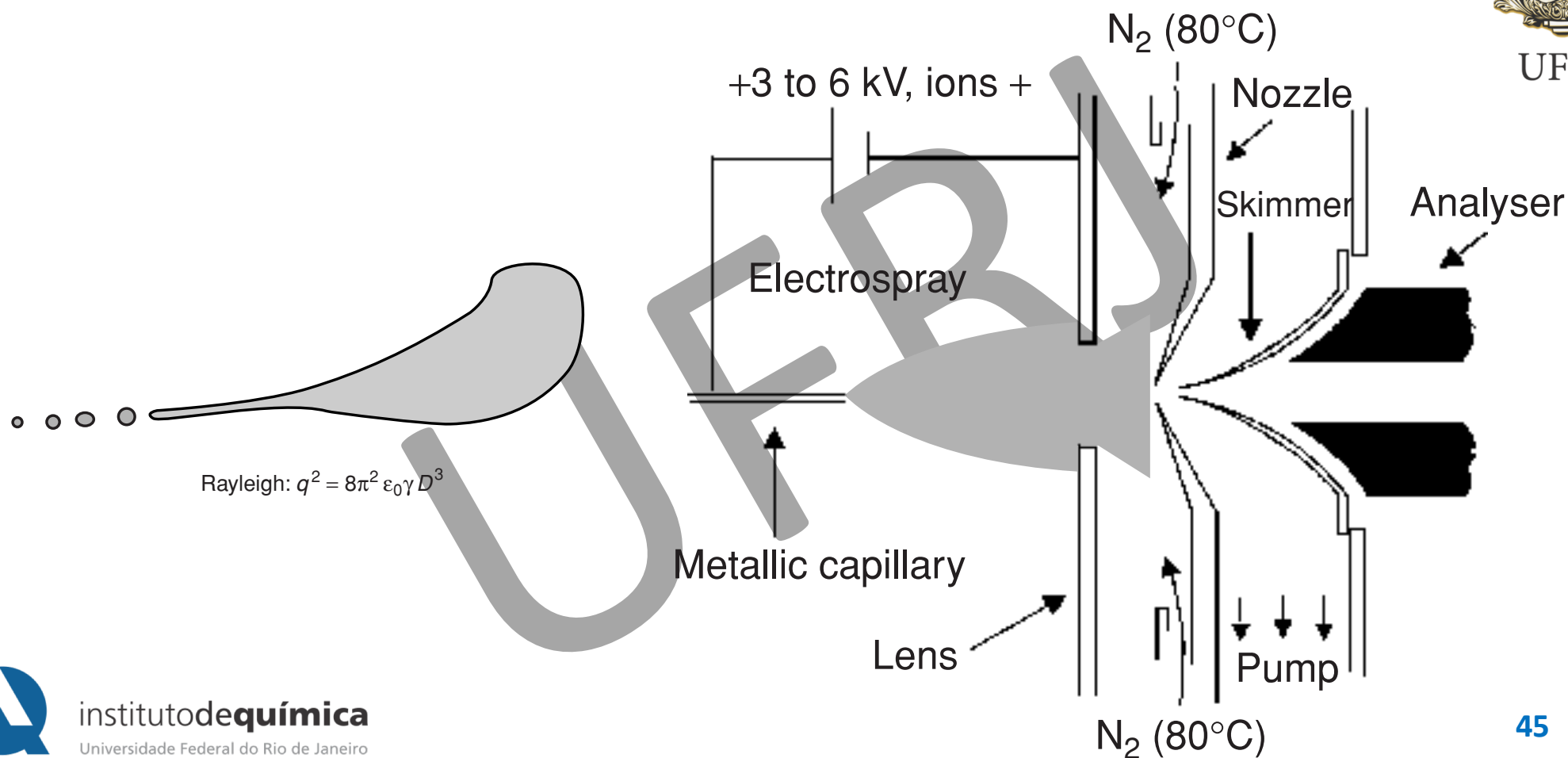
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Eletronspray



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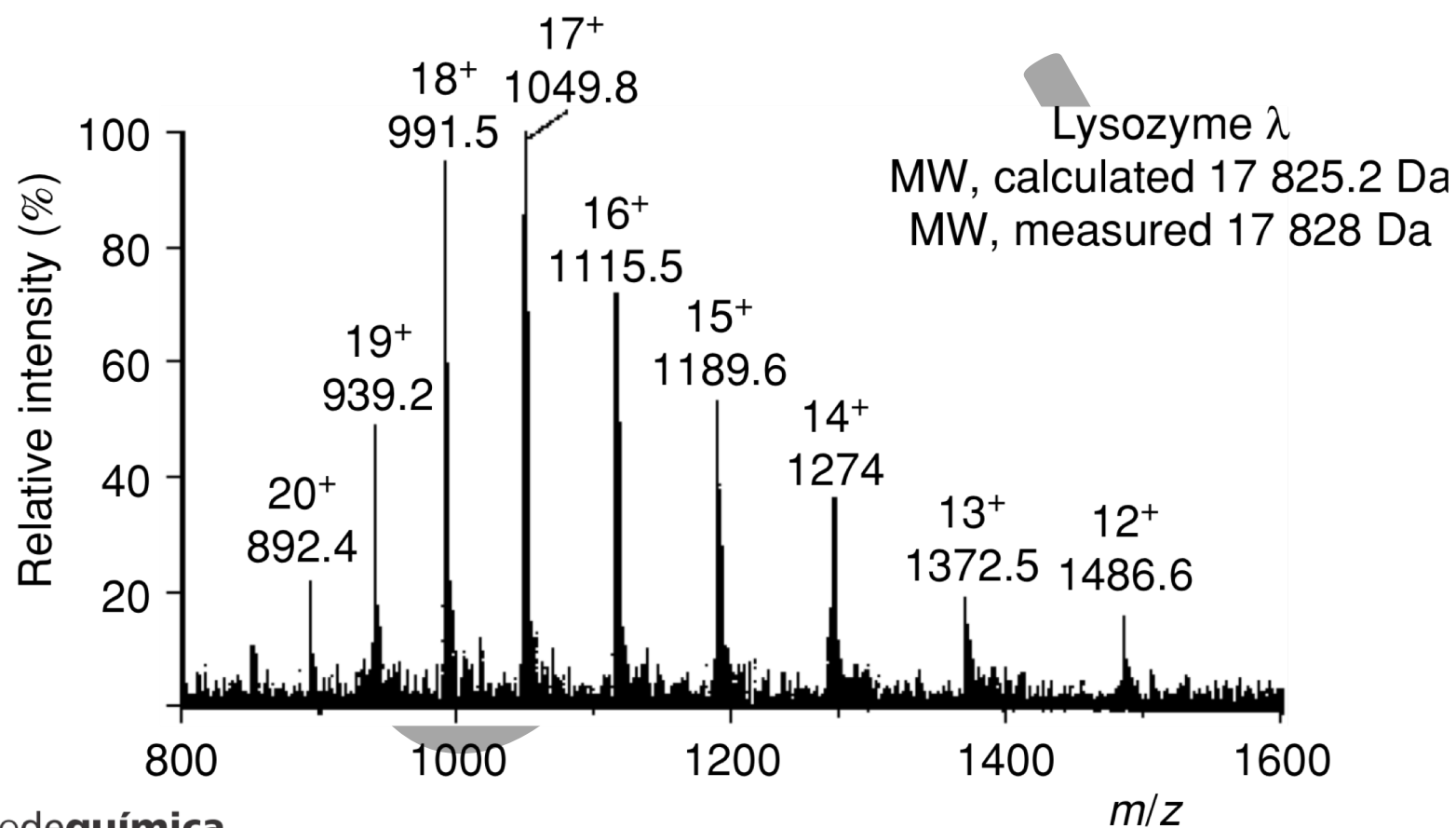


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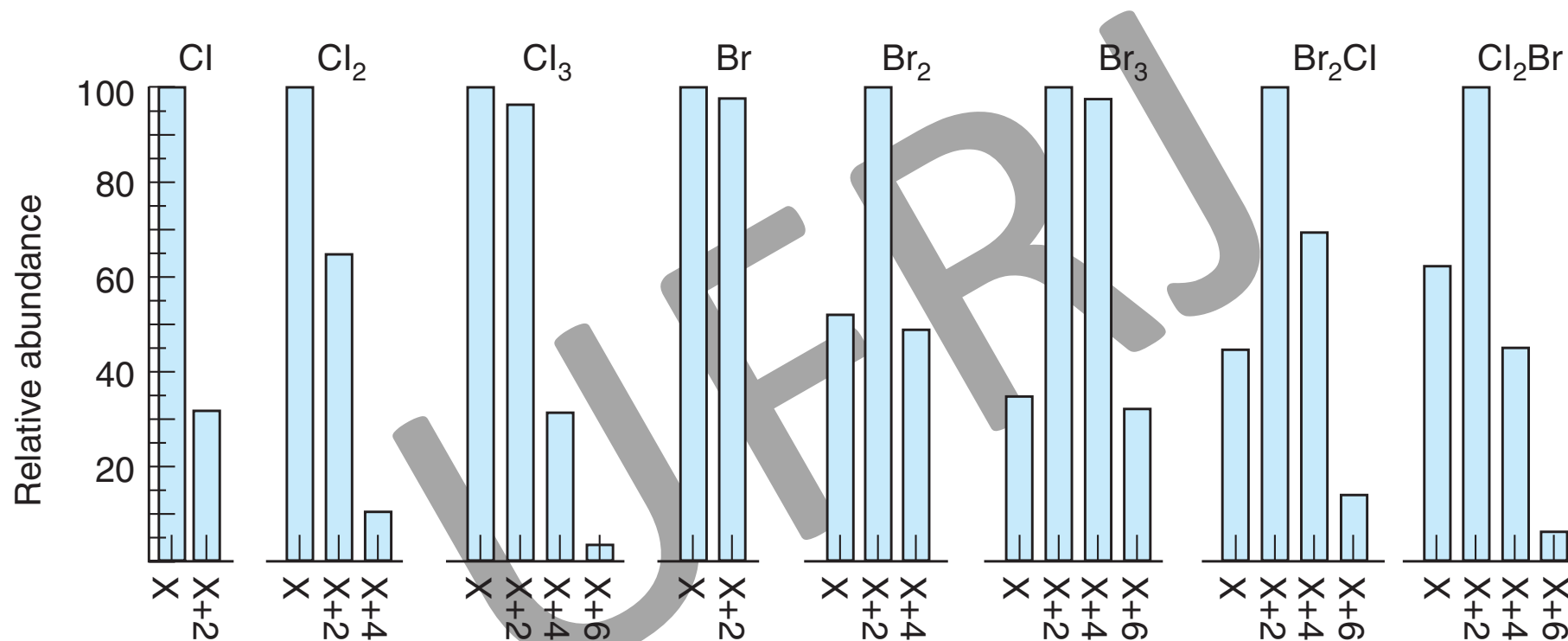
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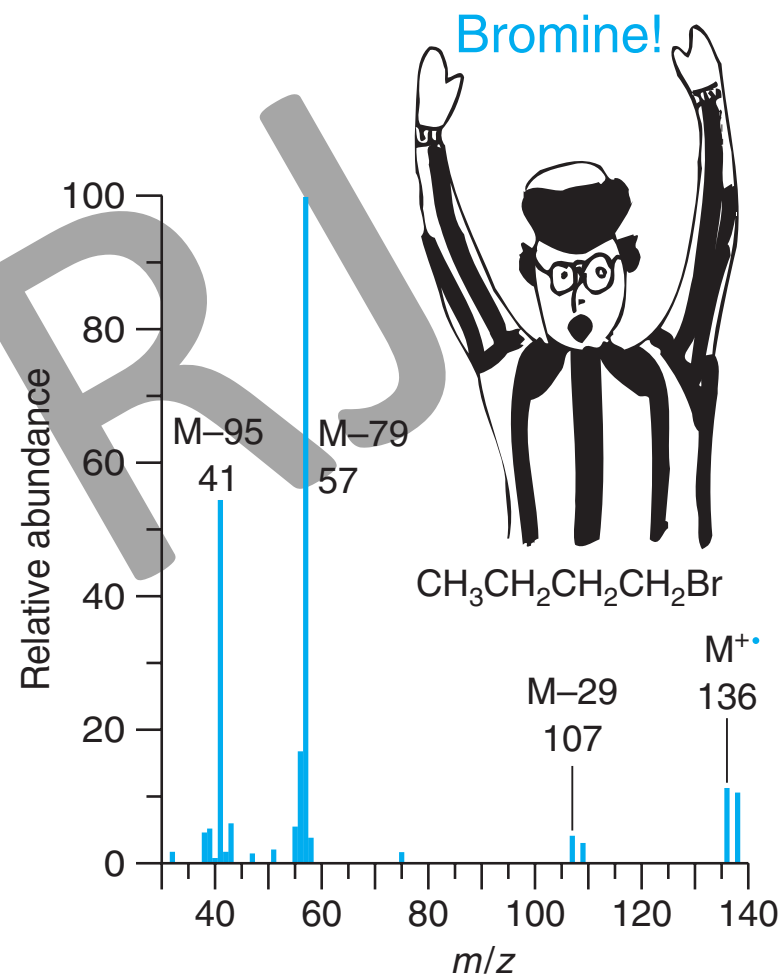
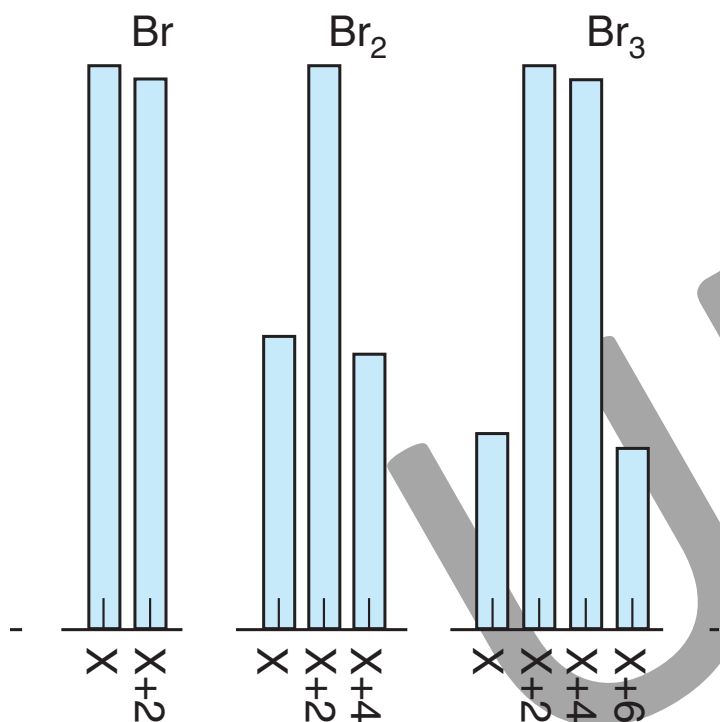
Isótopos ajudando no Espectro de Massas



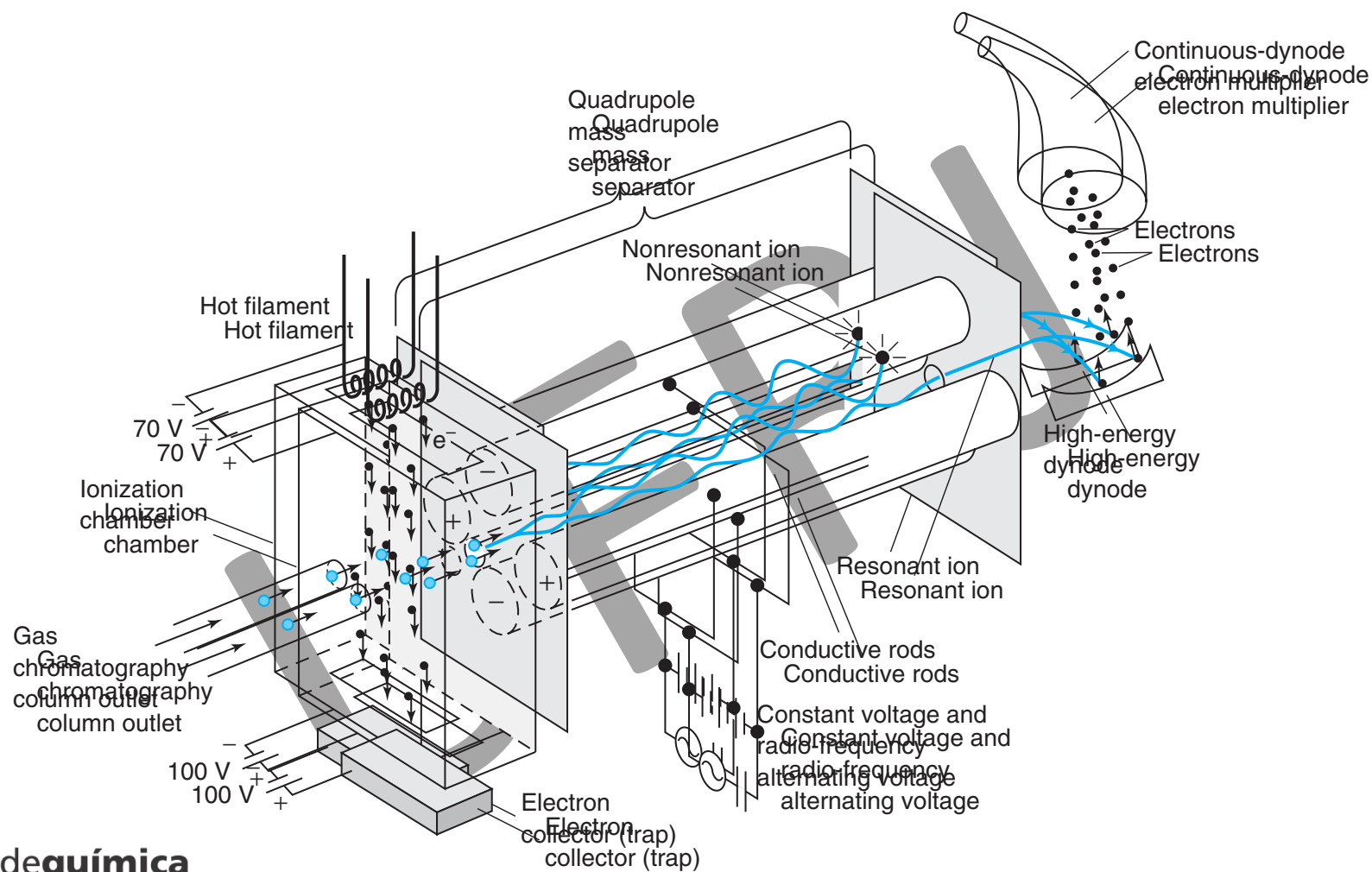
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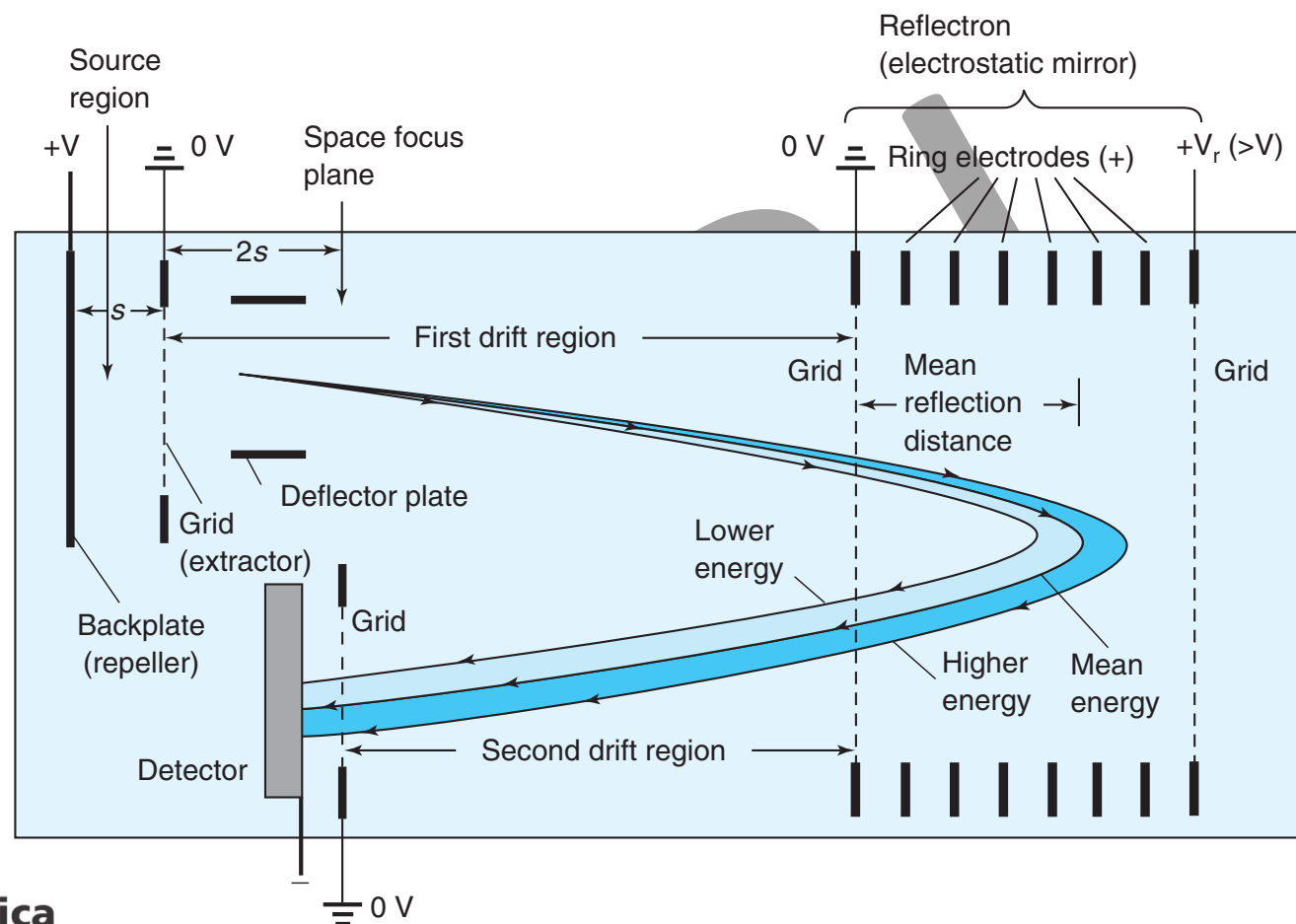
Isótopos ajudando no Espectro de Massas



Tipos de espectrômetros



Tipos de espectrômetros



Quebras moleculares

