QFL 1345 – Fundamentos de Espectroscopia e Métodos Espectroscópicos

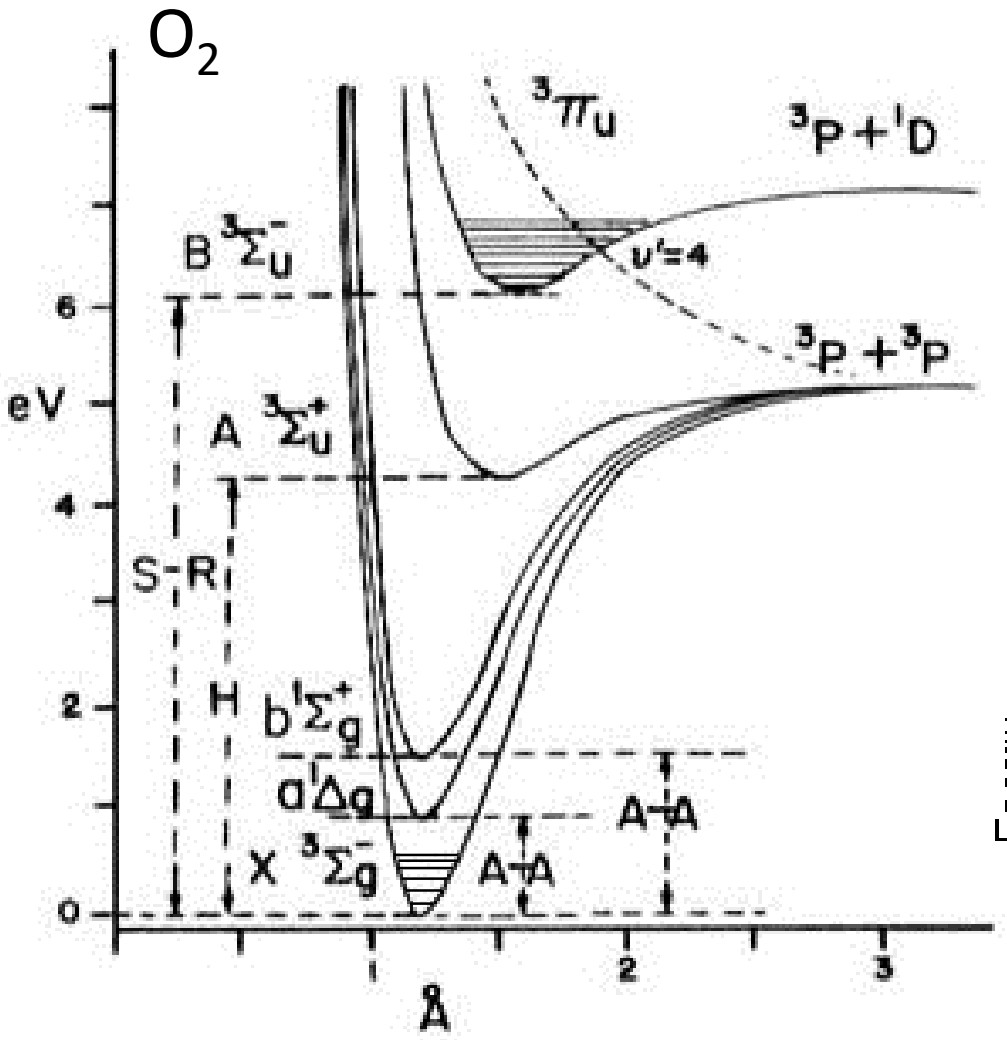
Espectrometria de massas

- Fundamentos
- Interpretação de espectros!

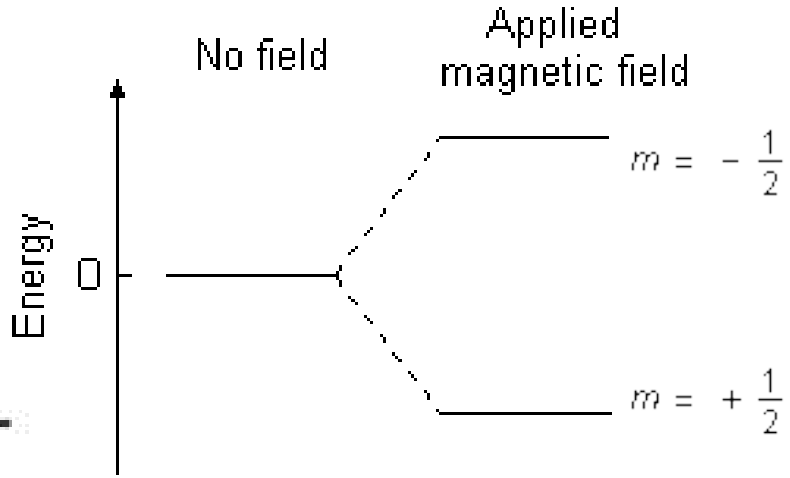
O que é a espectrometria de massas?

No que ela difere das outras espectroscopias?

Espectroscopias



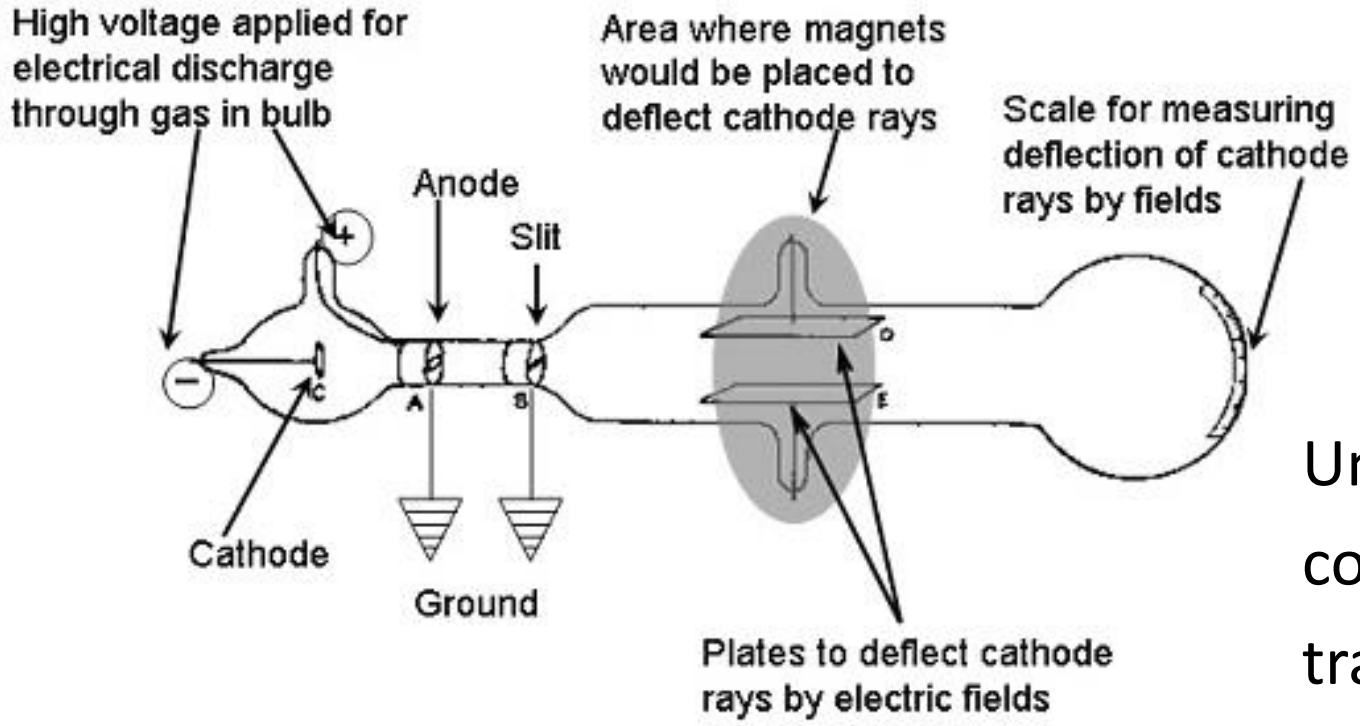
- UV-Vis
- Vibracional
- RMN
- Fotoquímica



"Dissociation Energies and the Spectra of Diatomic Molecules", Gaydon, 3rd ed, 1968, p.74
https://www.ems.psu.edu/~brune/m532/m532_ch3_photochemistry_fundamentals.html

Espectrometria de massas

- J.J. Thomson – Identificação do elétron (1897)
  - Nobel de física em 1906



Uma partícula com carga tem trajetória definida por massa/carga

Thomson, J.J. Phil. Mag. 1987, 44, 293

Espectrometria de massas

- J.J. Thomson – Identificação do elétron (1897)
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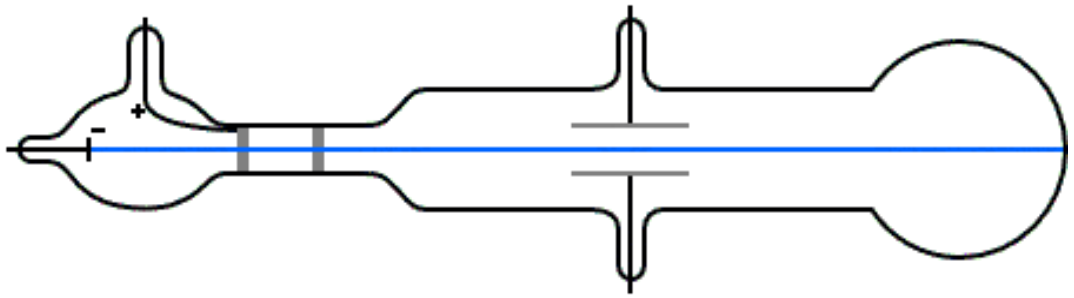
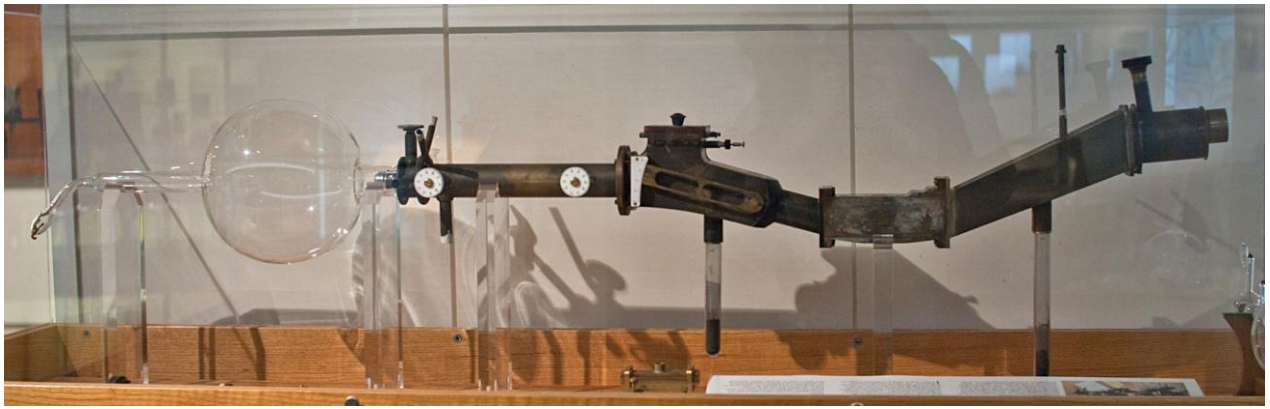


Uma partícula com carga tem trajetória definida por massa/carga

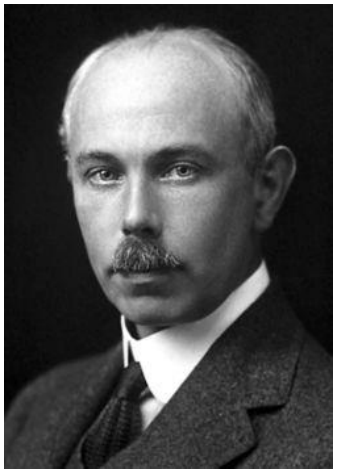
Thomson, J.J. Phil. Mag. 1897, 44, 293

Espectrometria de massas

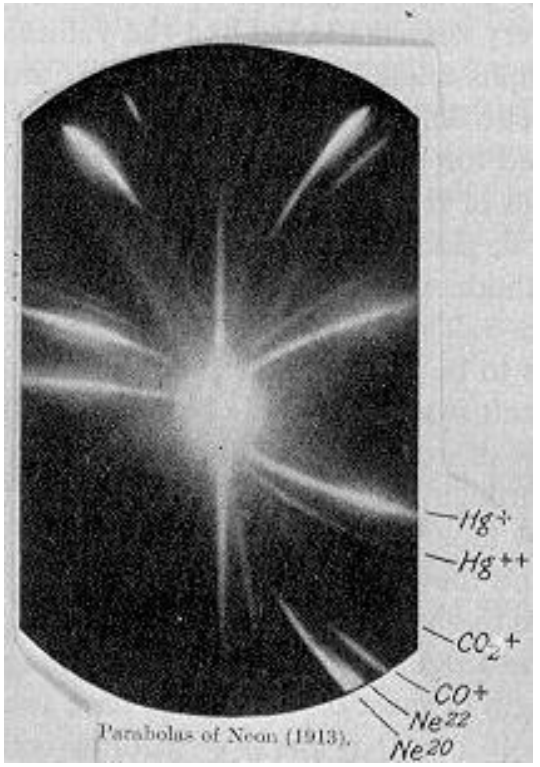
- Aston e Dempster – Melhoramentos e medidas de outras partículas



Espectógrafo de massas

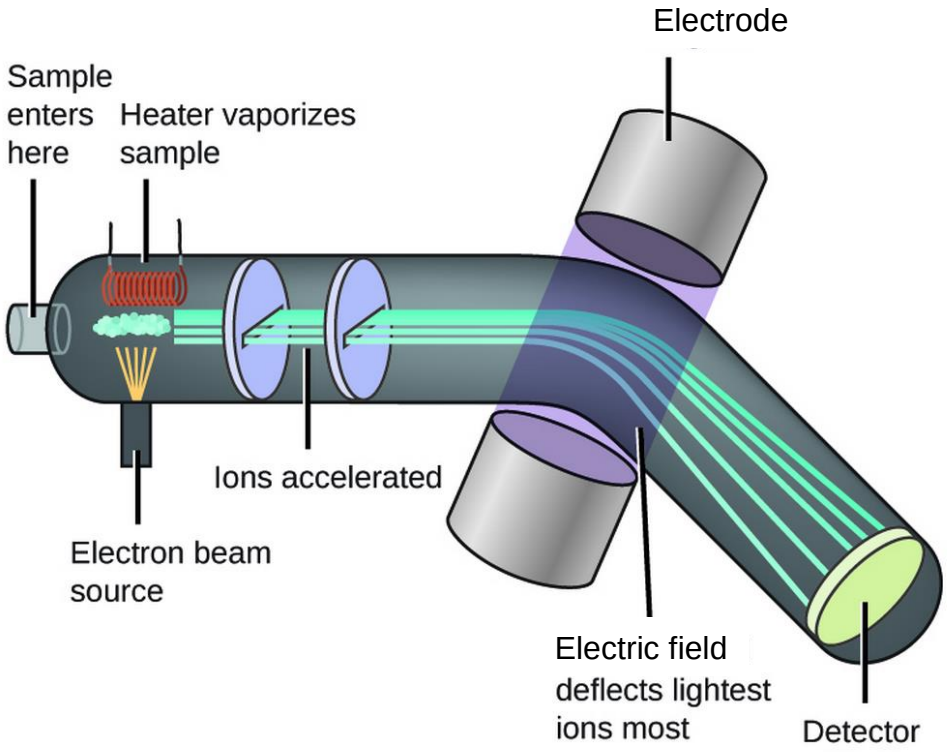


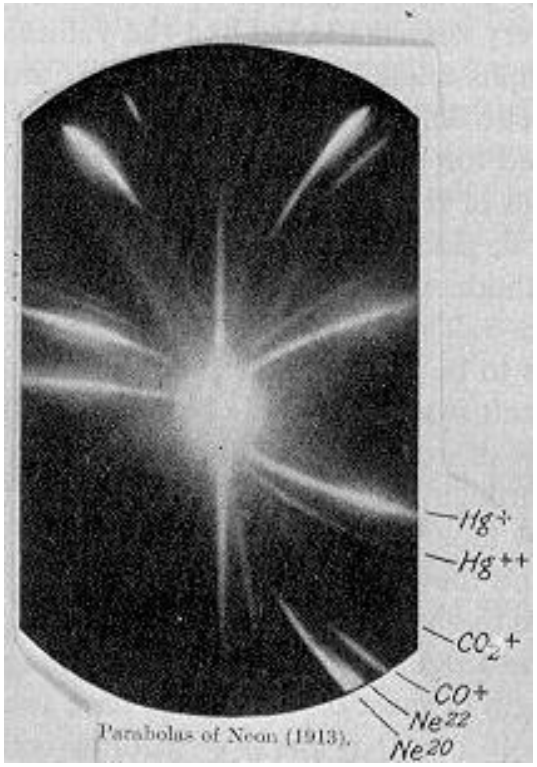
F. A. Aston
Premio Nobel
1922
Química



Espectrometria de massas

- Aston e Dempster – Melhoramentos e medidas de outras partículas

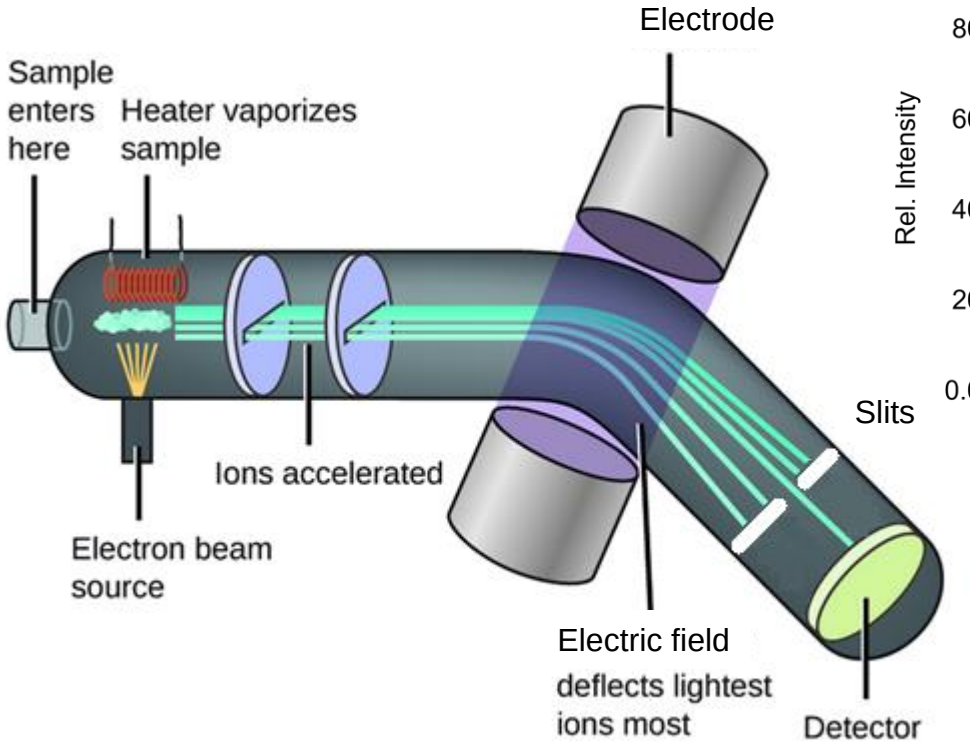




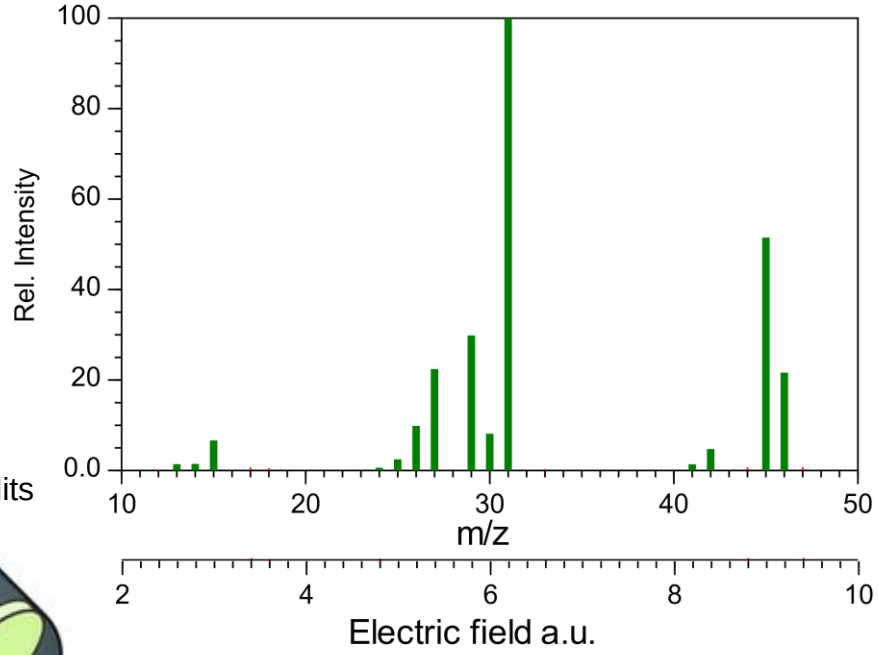
https://www.khanacademy.org/science/chemistry/atomic-structure-and-properties/mass-spectrometry/a/isotopes-and-mass-spectrometry

Espectrometria de massas

- Aston e Dempster – Melhoramentos e medidas de outras partículas



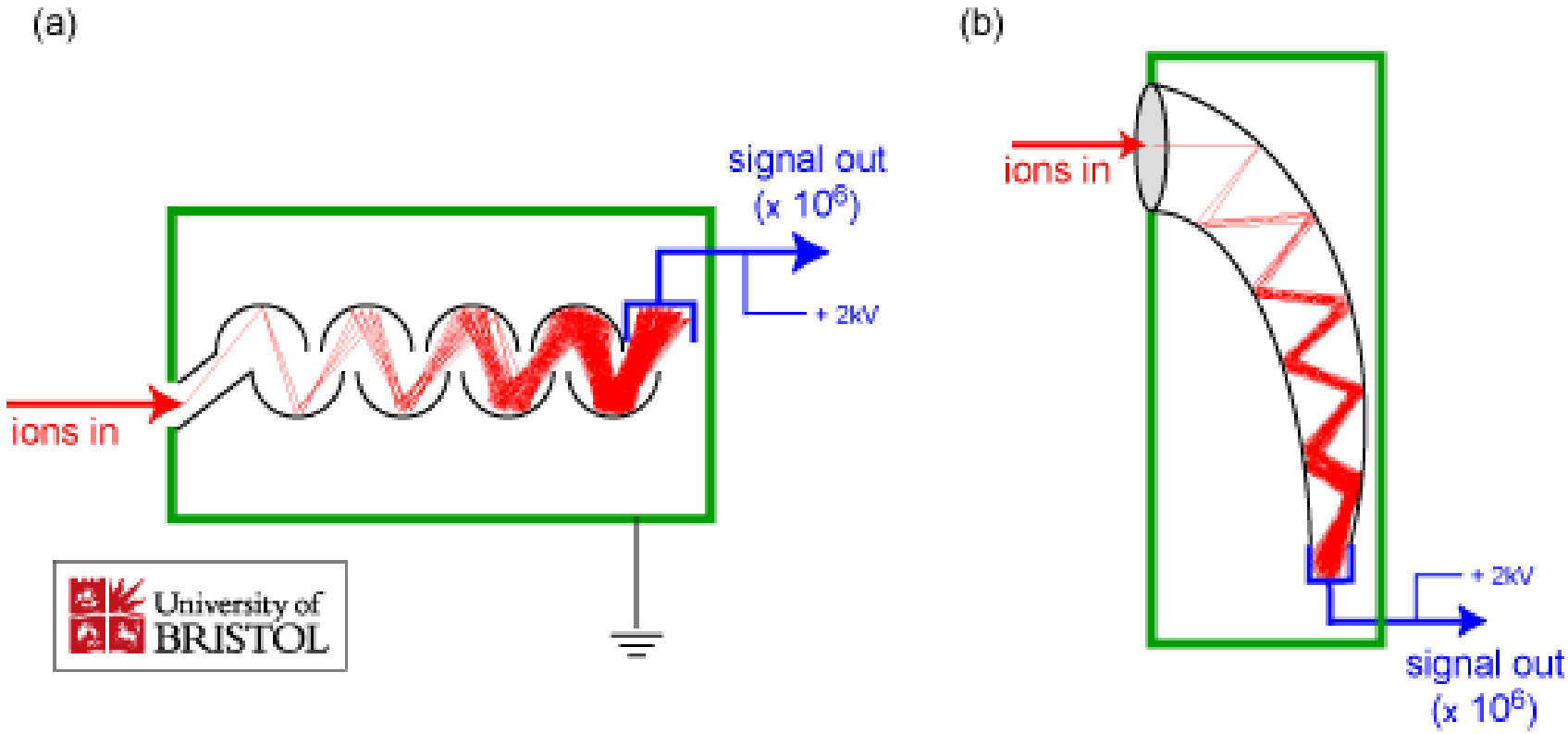
Espectrômetro de massas



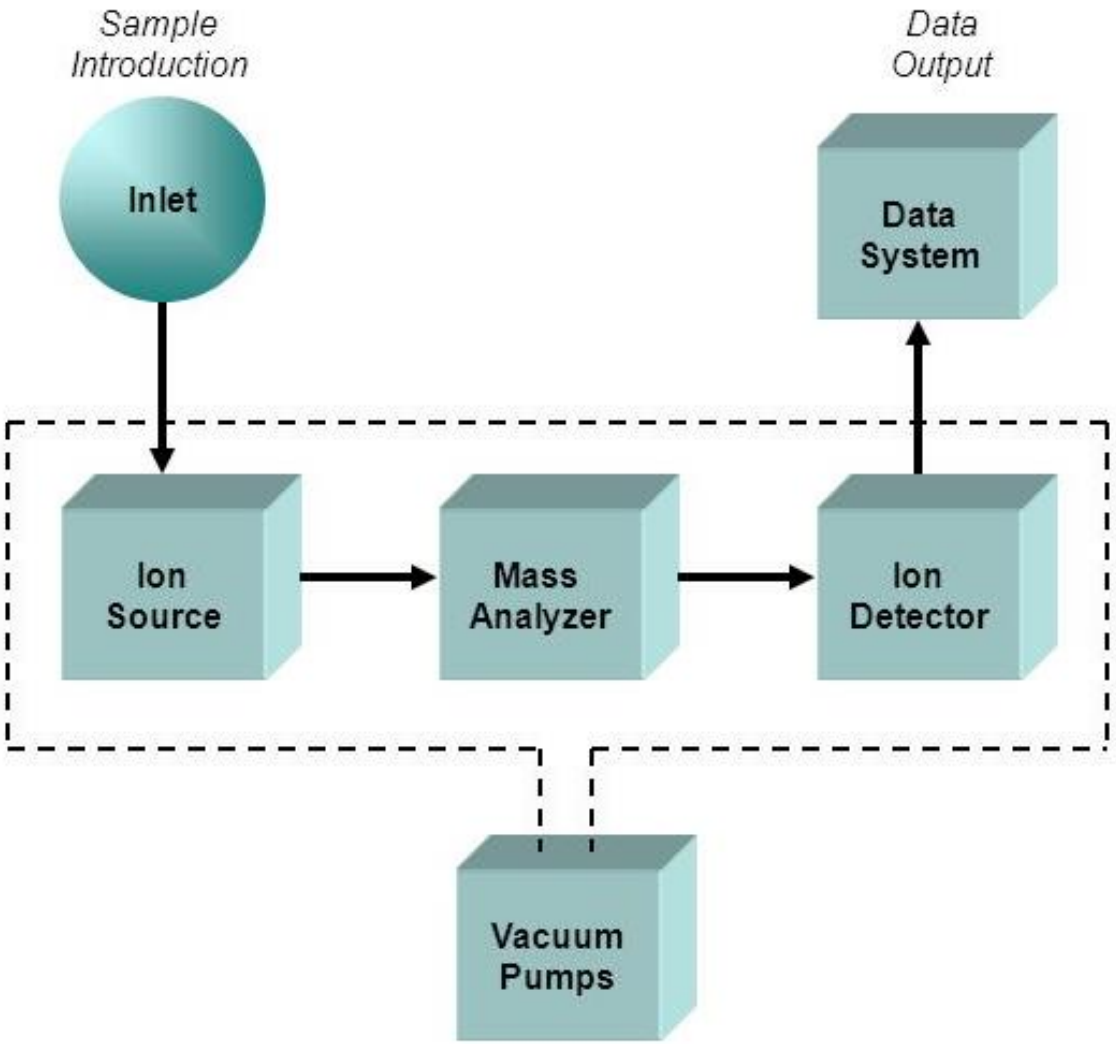
Quantidade de cada íon determinada individualmente

https://www.khanacademy.org/science/chemistry/atomic-structure-and-properties/mass-spectrometry/a/isotopes-and-mass-spectrometry

Detectores de íons



Espectrômetro de massas moderno



- Introdução de amostra
- Fontes de Ionização
- Analisador de massas
- Detector

http://slideplayer.com/slide/6537508/

Características da espectrometria de massas

- Universal
- Rápida
- Precisa
- Seletiva
- Sensível
- Identificação
- Quantificação
- Miniaturizável
- Robusta
- Interfaceável
- Automatizável
- Para todos os bolsos!

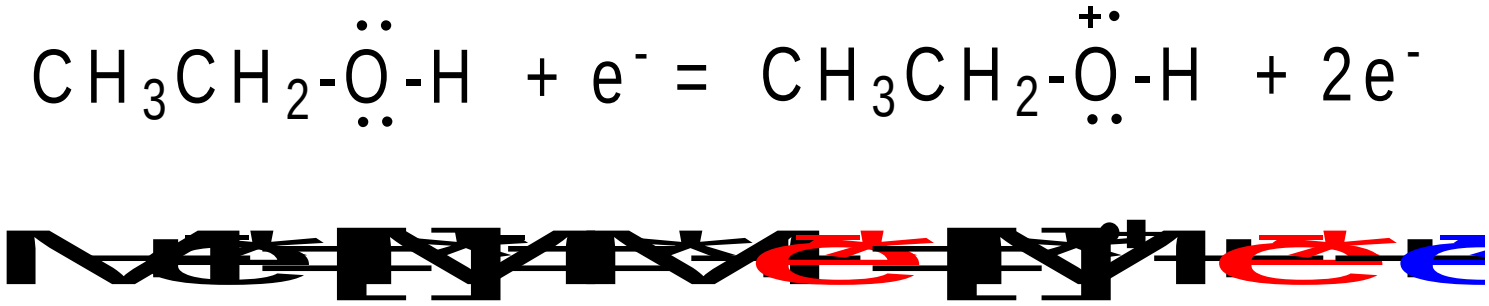
Equipamentos diferentes para usos diferentes!

Objetivo: Aprender a ler e interpretar espectros de massa!

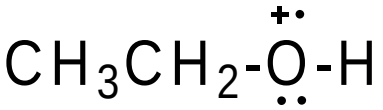
Entender fontes de íons e seletores de massa distintos!

Ionização por elétrons (ou Impacto eletrônico)

Caso do Etanol:



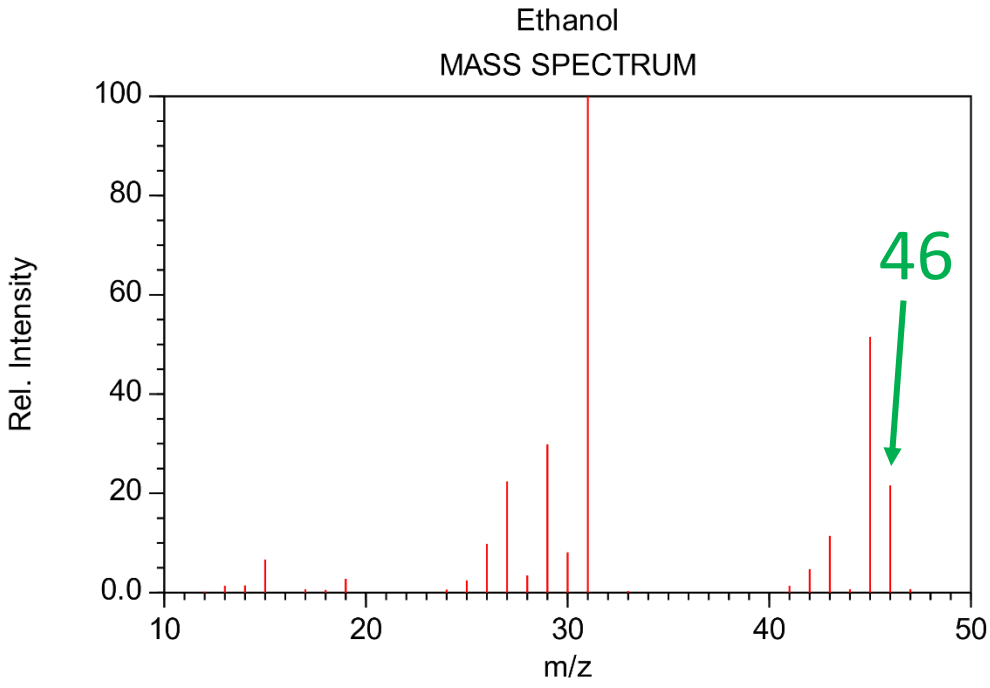
70 eV = 1610 kcal/mol!



Massa (m): 46 Da

Carga (z): +1 a.u

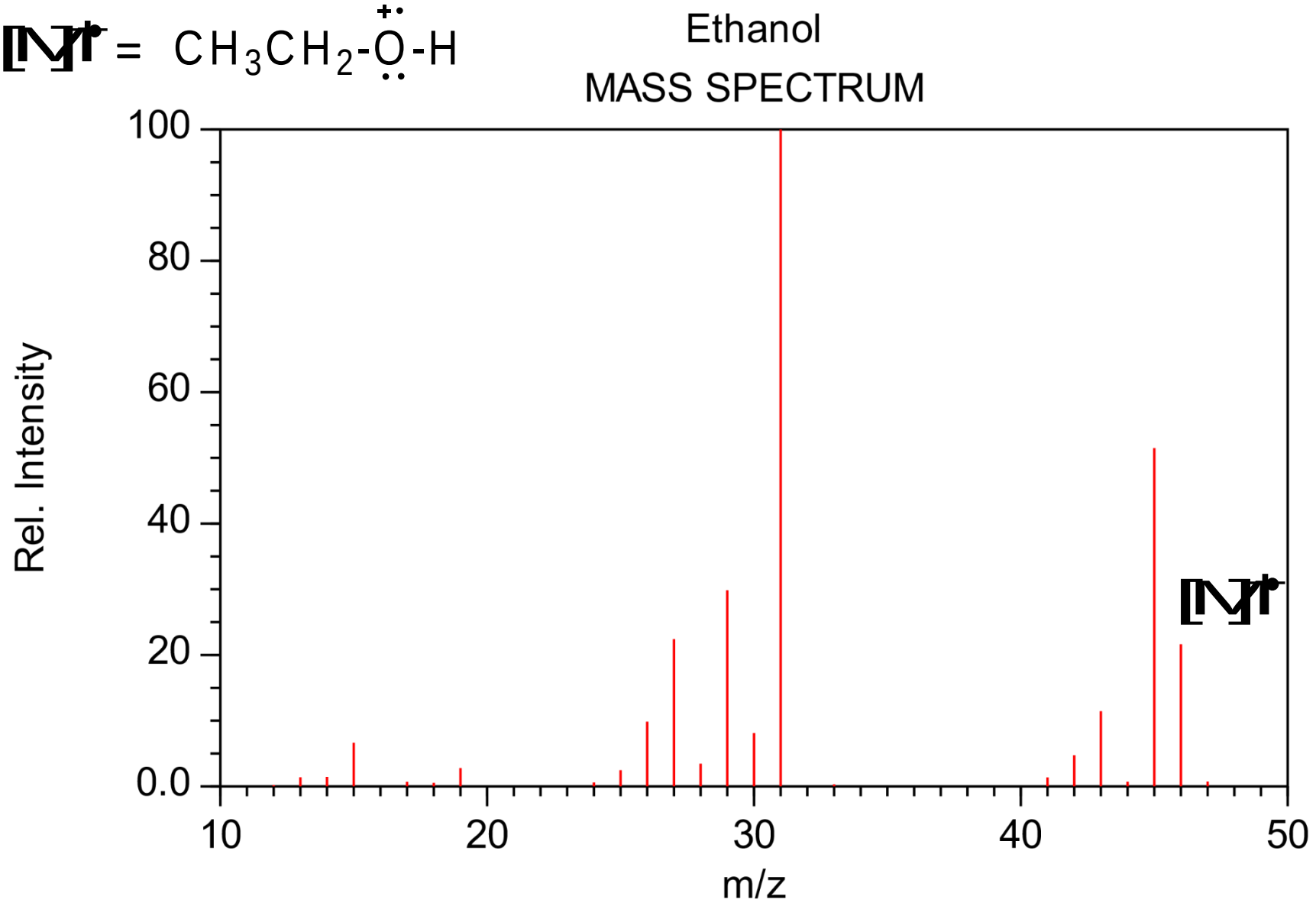
***m/z* 46** Th (não costuma ser utilizada!)



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Fragmentação

$[M]^{+\bullet}$ = CH_3CH_2-$\ddot{O}^{+\bullet}$-H



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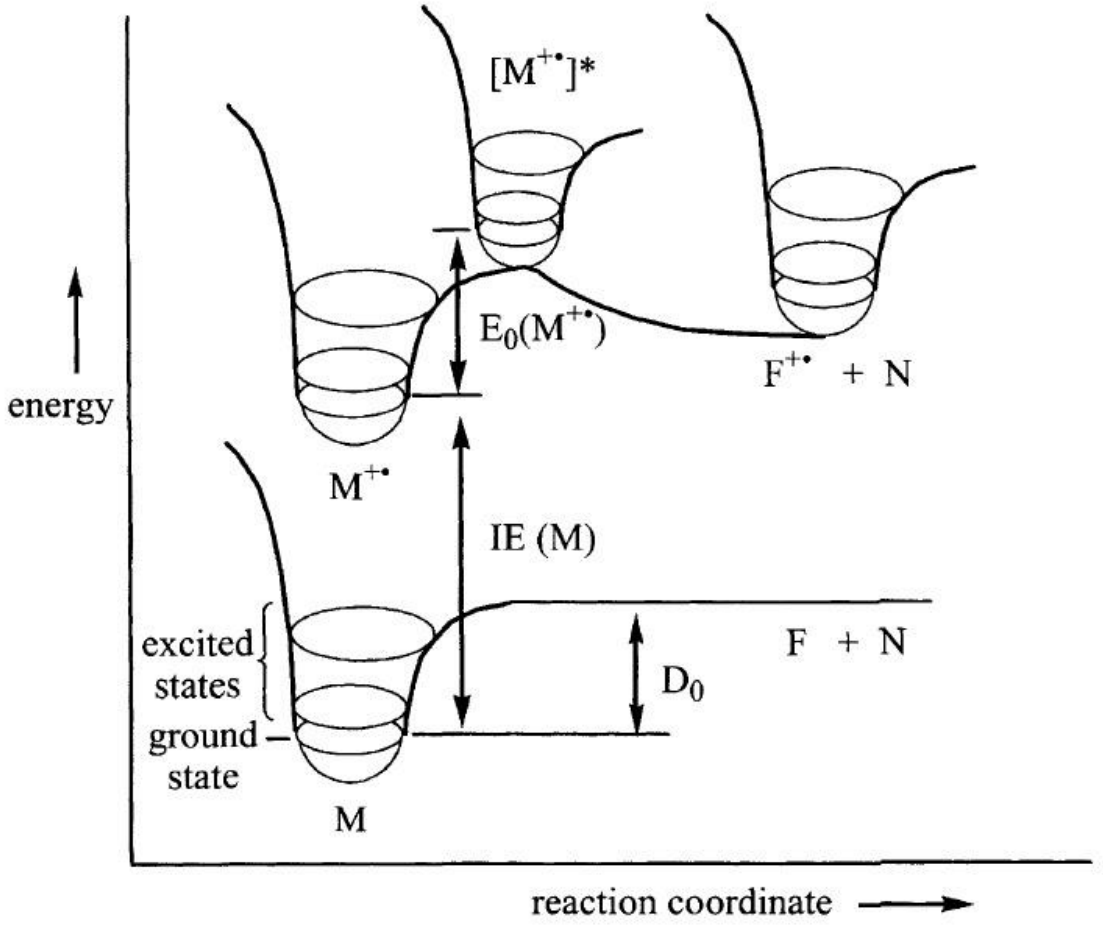


Fragmentação:

$$[M^*]^{+\bullet} = F^+ + R^\bullet$$

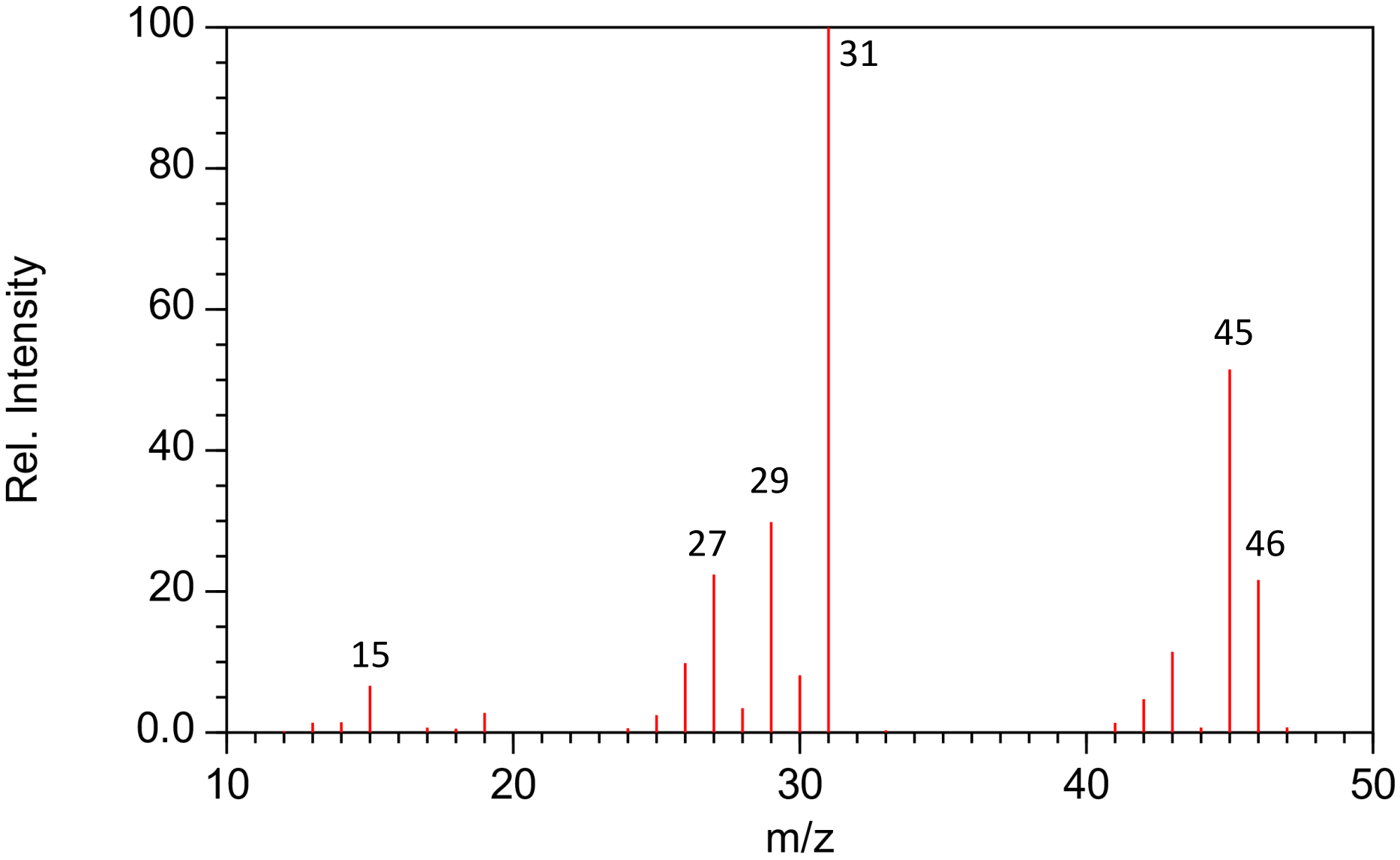
ou

$$[M^*]^{+\bullet} = F^{+\bullet} + N$$

(menos comum)

Ionização por elétrons gera muitos fragmentos

Etanol



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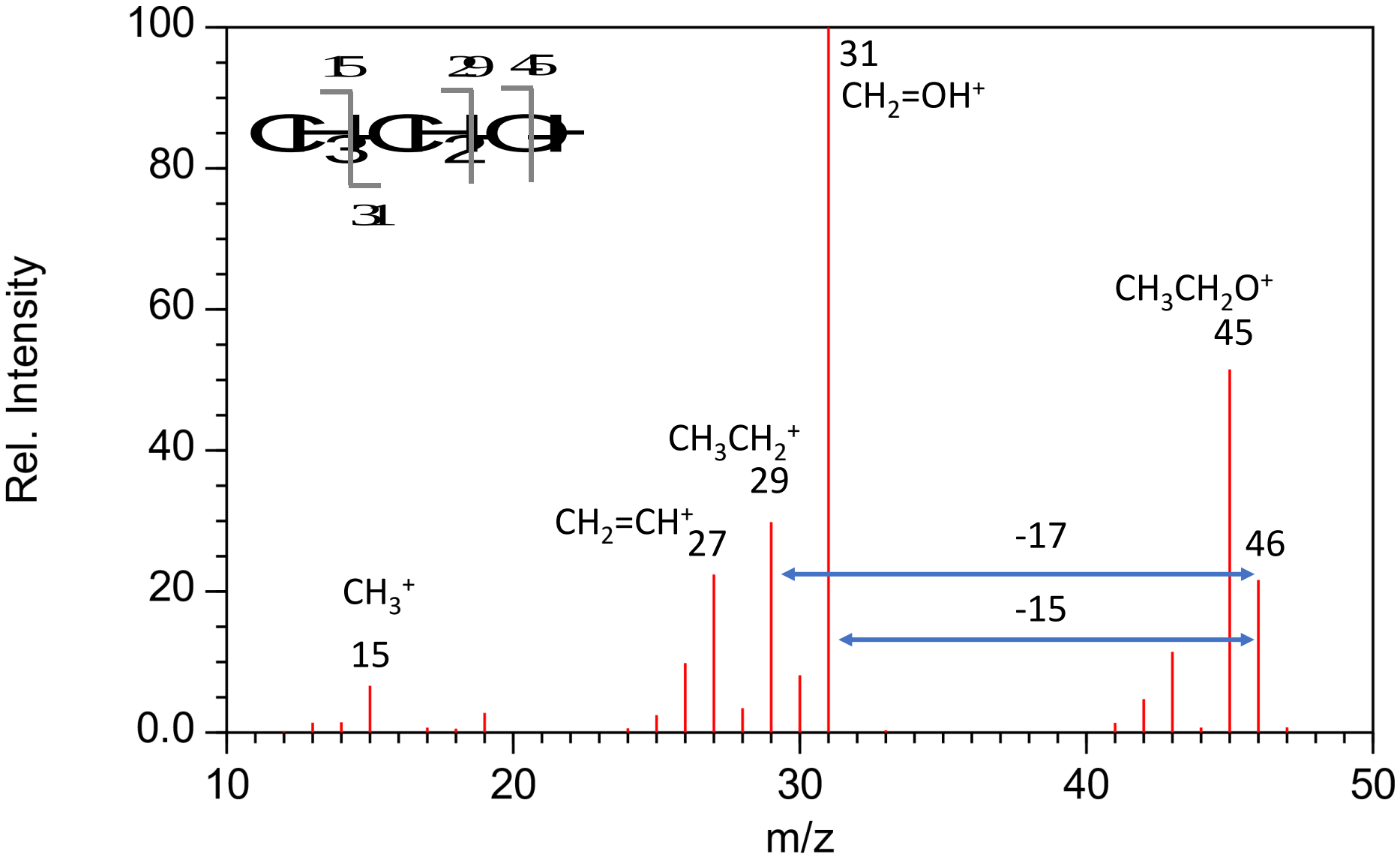
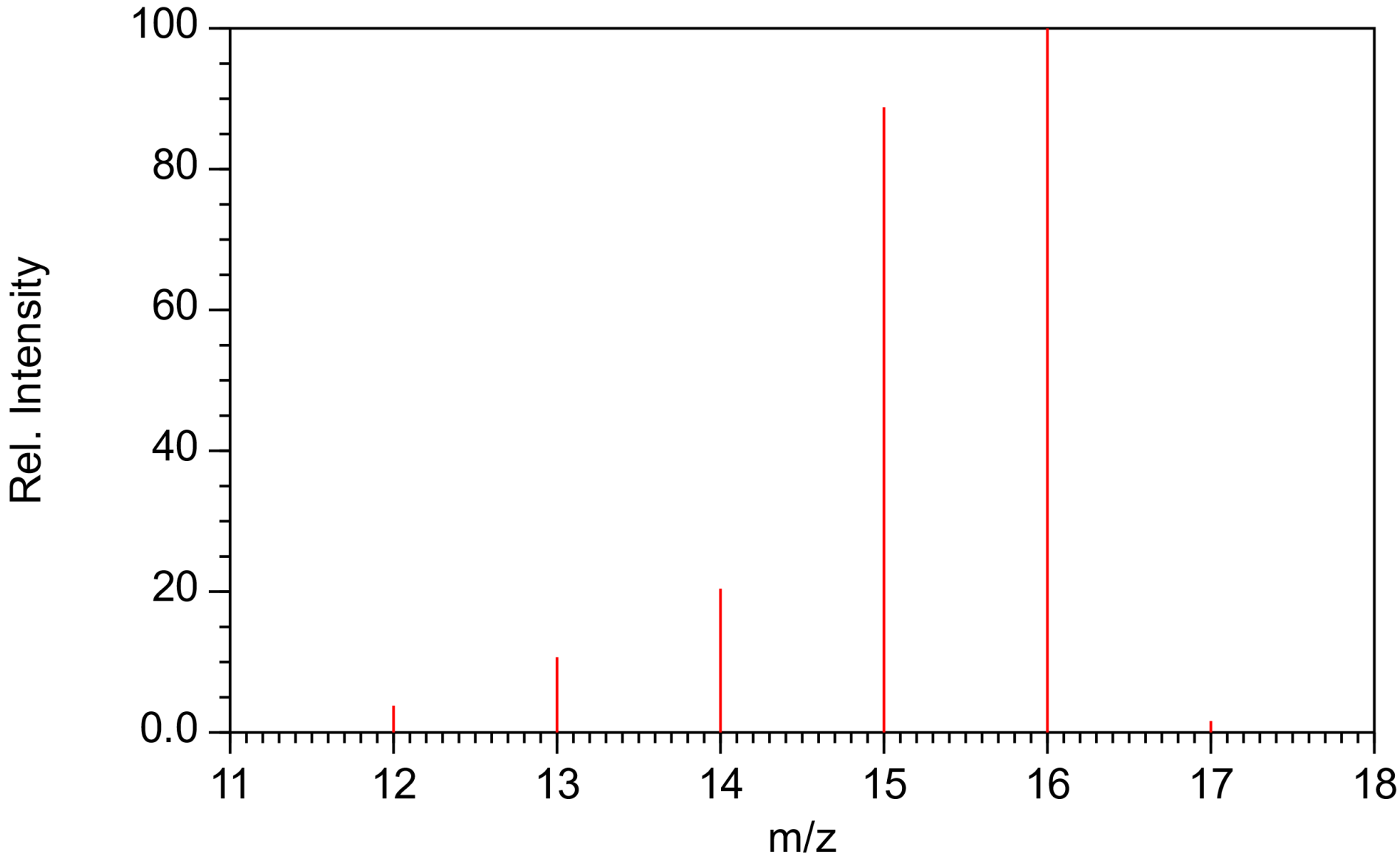
Etanol



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Metano



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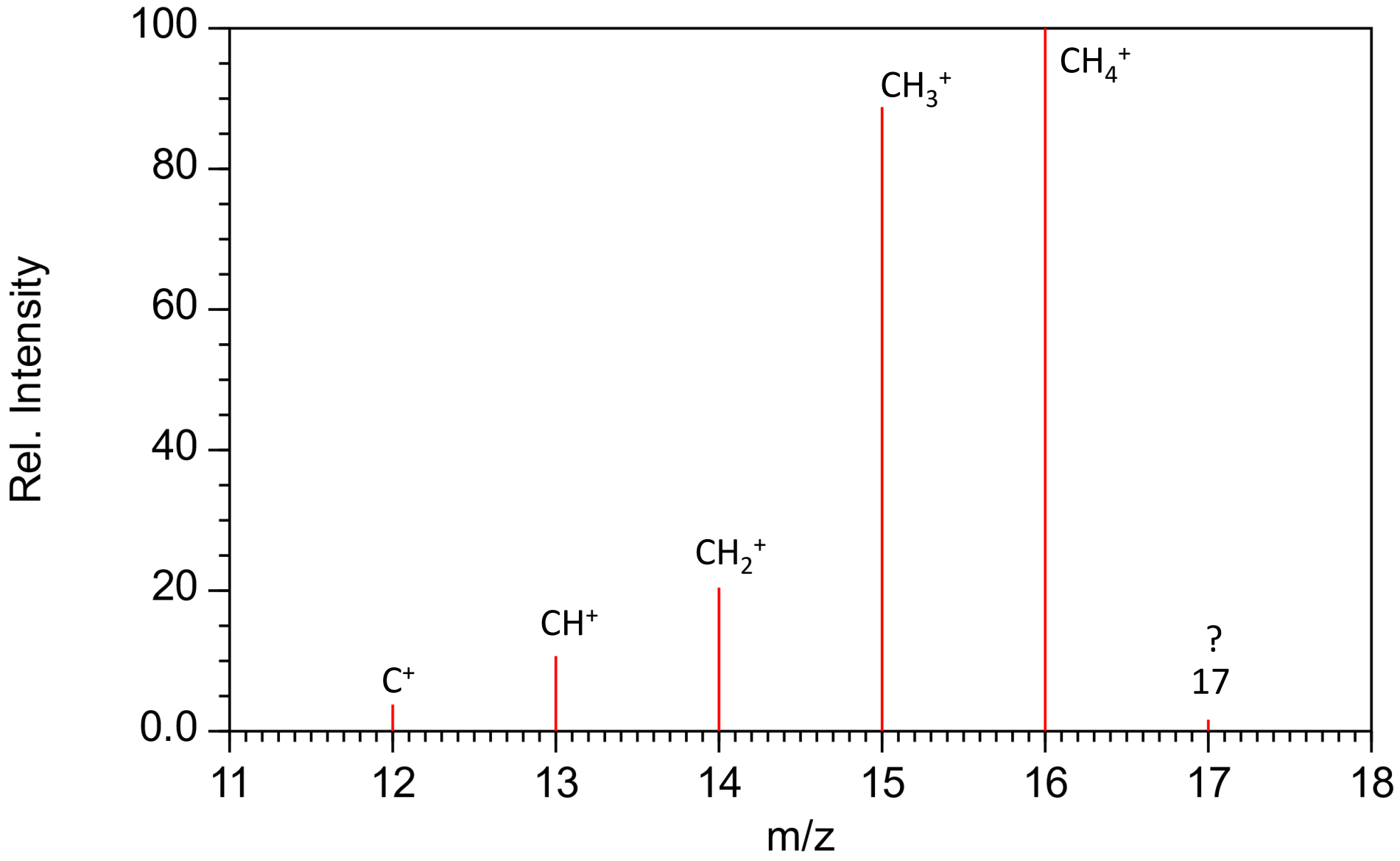
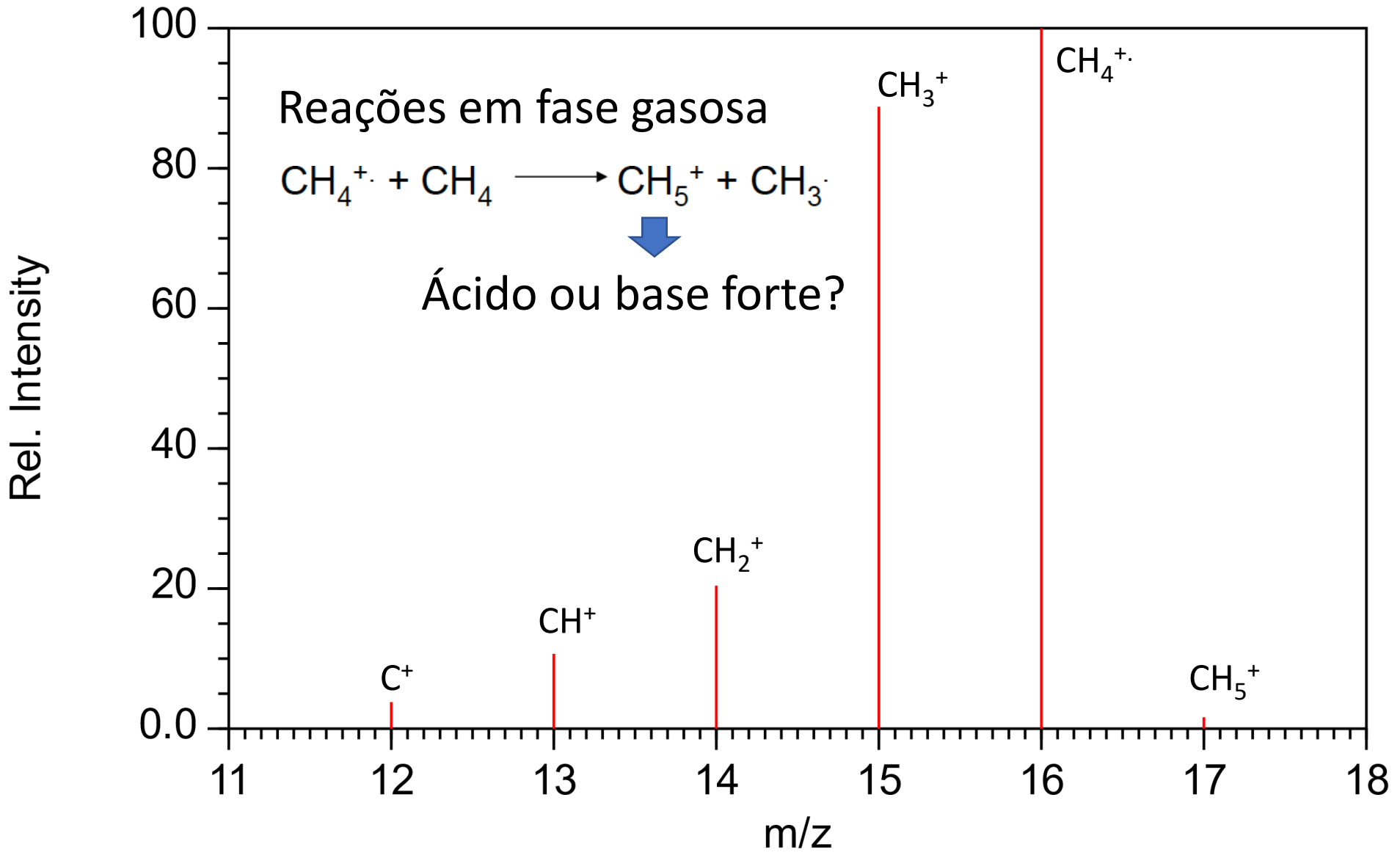
Metano



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Metano



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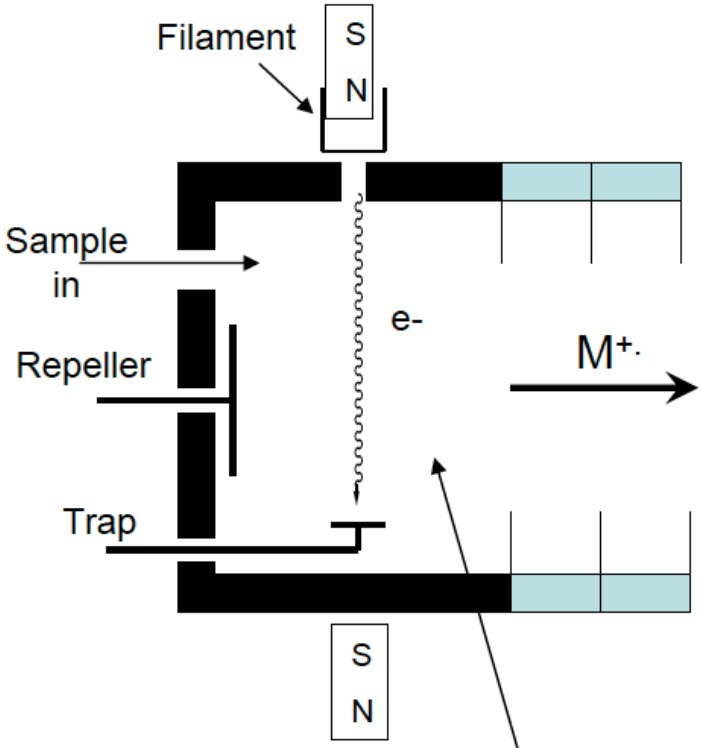
EI Source

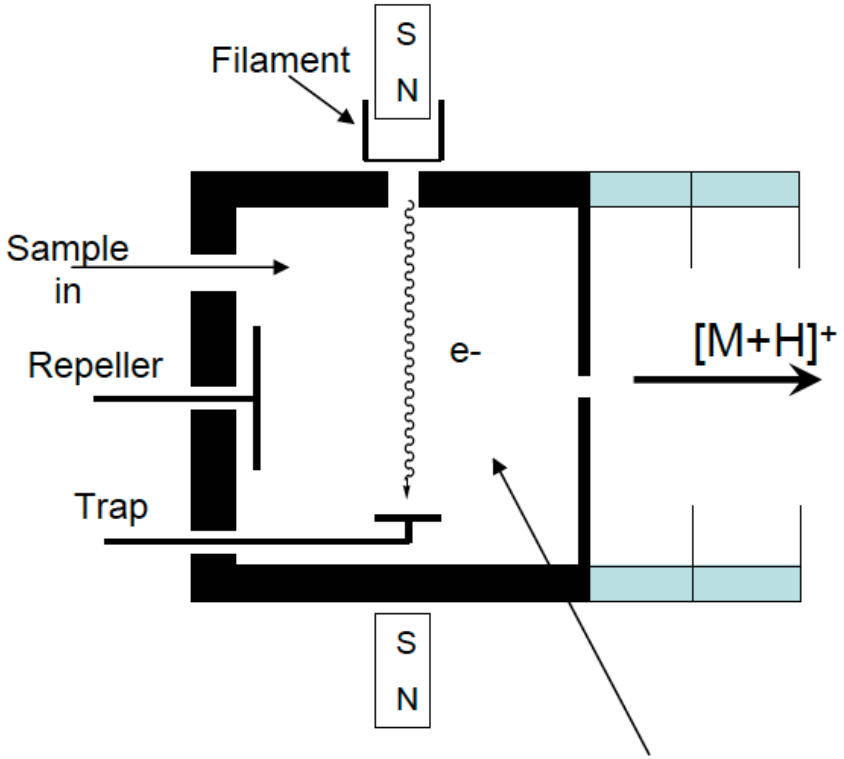


Source pressure ~ 10^{-6} Torr

$$M + e^- \rightarrow [M]^{+\cdot} + 2e^-$$

Fragmentos!

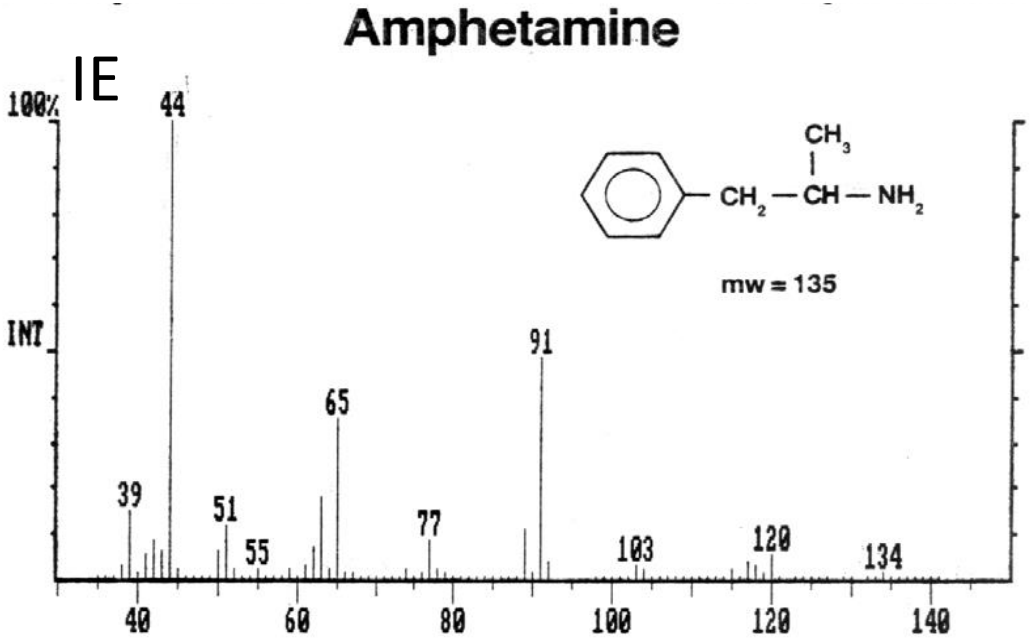
CI Source

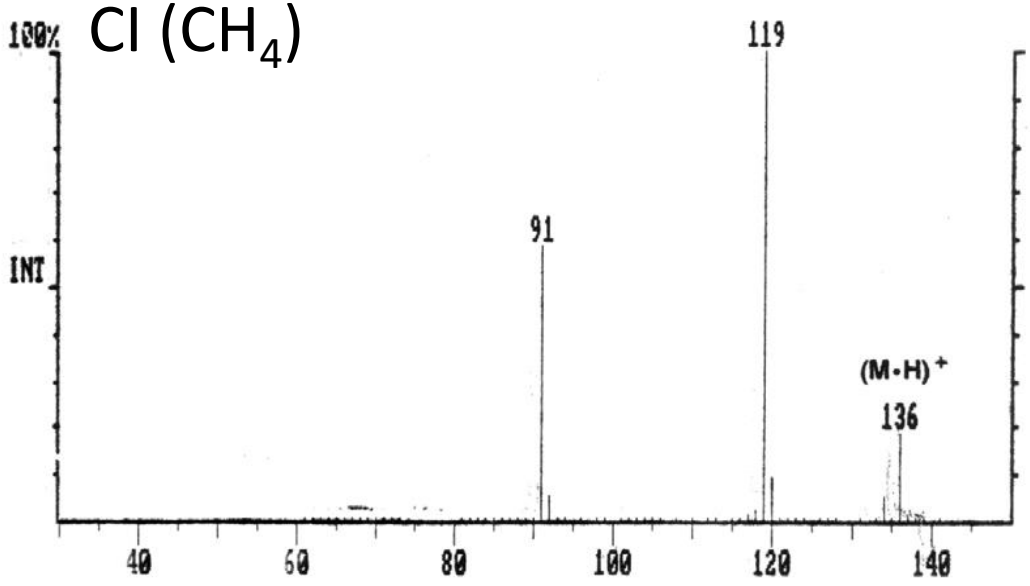


Source pressure ~ 0.1-1 Torr

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3^{\cdot}$$

$$CH_5^+ + M = CH_4 + [M+H]^+$$





$$Me^{+} + [M]^{+} + 2e^{-}$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^{+} + CH_3^{\cdot}$$

$$CH_5^{+} + M = CH_4 + [M+H]^{+}$$

Positive Ion Chemical Ionization

Formation of reagent ions depends on pressure and residence time:

Methane:

$CH_4 + e^- \longrightarrow CH_4^{+\cdot} + 2e^-$

$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3^{\cdot}$

$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$

$CH_5^+ + M \longrightarrow MH^+ + CH_4$

Ammonia:

$NH_3 + e^- \longrightarrow NH_3^{+\cdot} + 2e^-$

$NH_3 + NH_3^{+\cdot} \longrightarrow NH_4^+ + NH_2^{\cdot}$

$NH_4^+ + M \longrightarrow MH^+ + NH_3$

$NH_4^+ + M \longrightarrow [M+NH_4]^+$

- **Transferência de próton depende da afinidade protônica relativa entre o substrato neutro e a base conjugada do ácido**

$M + H^+ \rightarrow MH^+$ AP (M) = $- \Delta H_o$

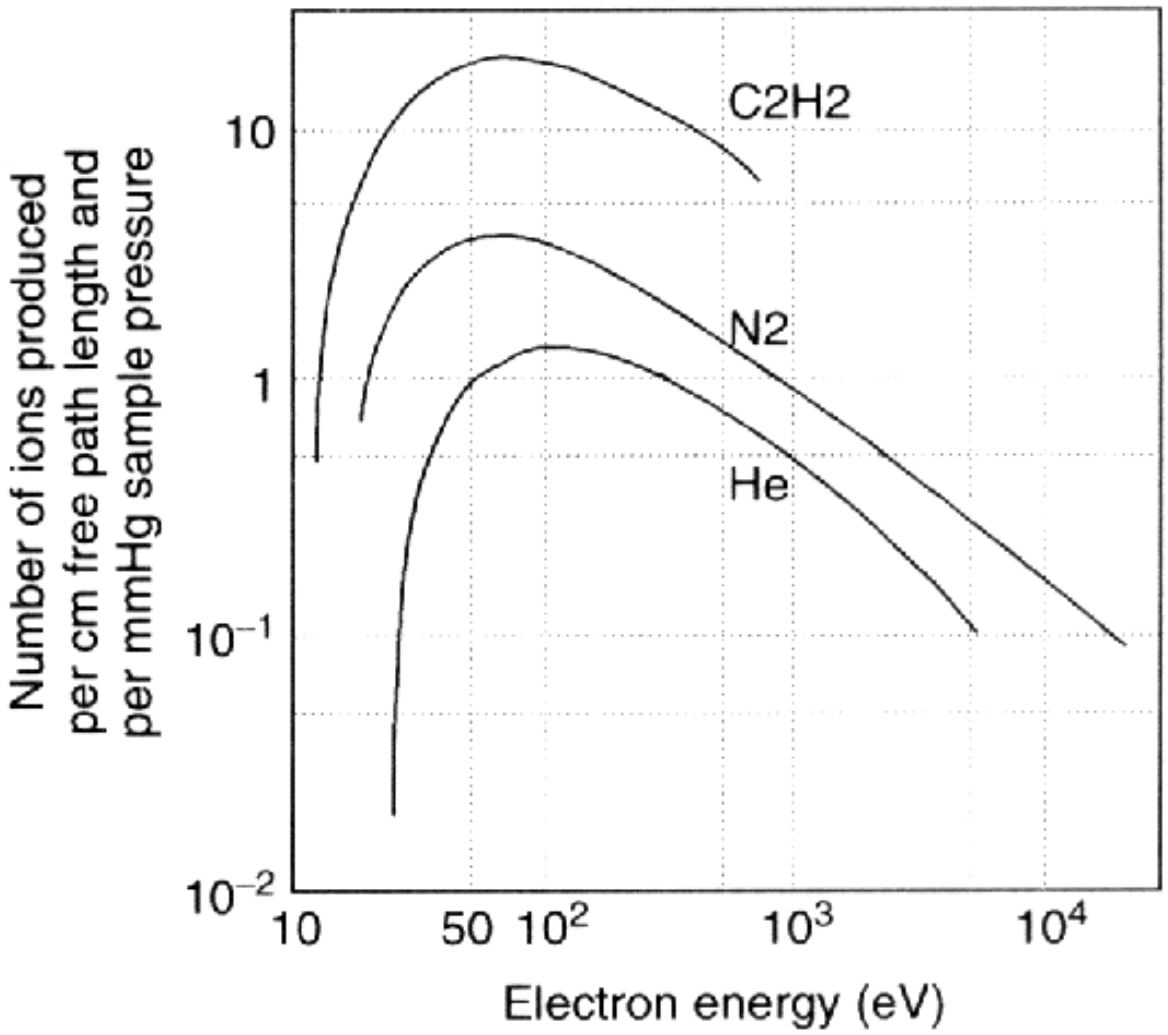
AP (CH_4) = 543,5 kJ mol^{-1}

AP (C_4H_8, isobuteno ou $Me_2C{=}CH_2$) = 802,1 kJ mol^{-1}

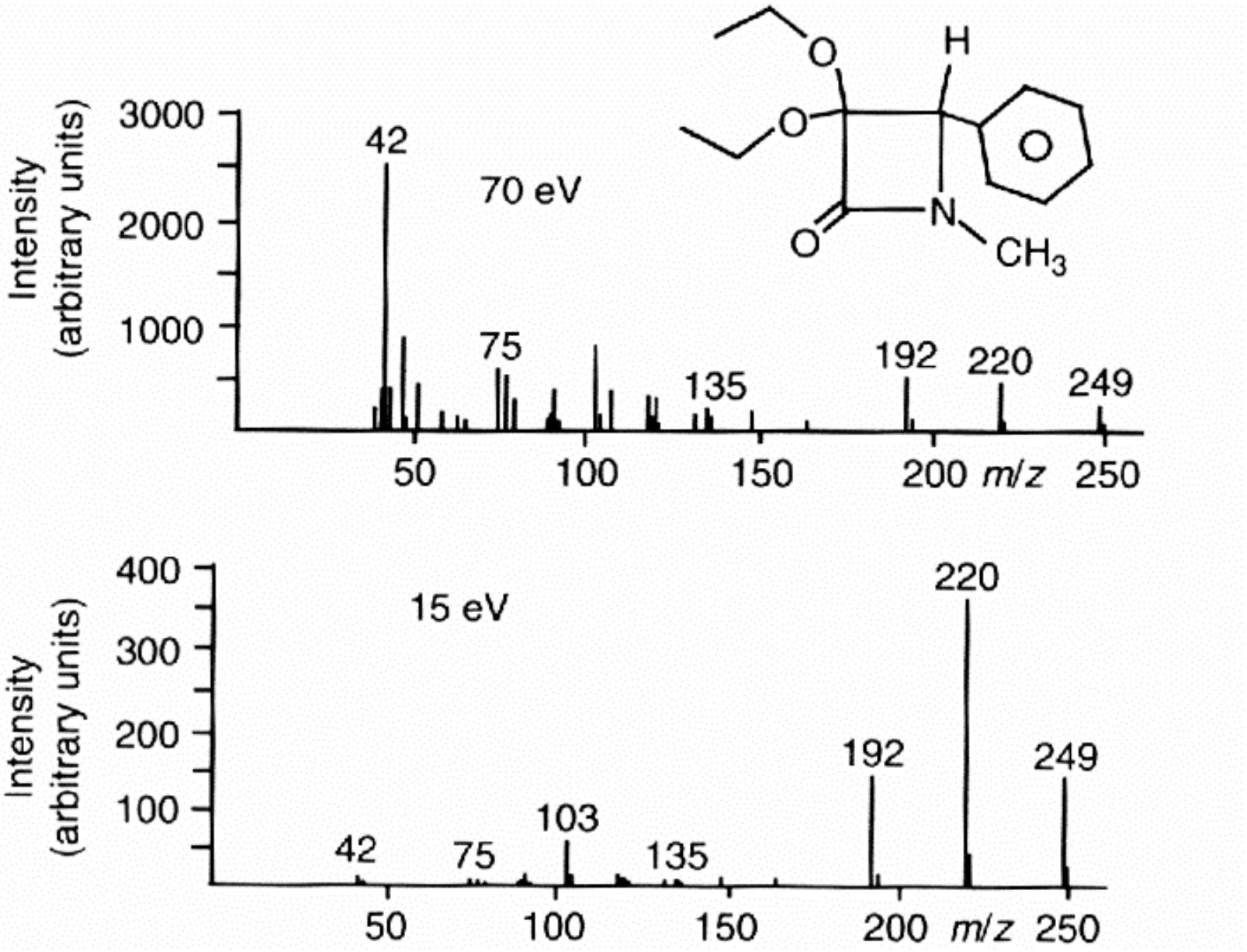
AP (NH_3) = 853,6 kJ mol^{-1}

Não seria possível utilizar elétrons menos energéticos?

Eficiência de ionização máxima ~ 70 eV



Espectros de massas de uma β-lactama a duas energias eletrônicas diferentes: maior fragmentação a 70 eV



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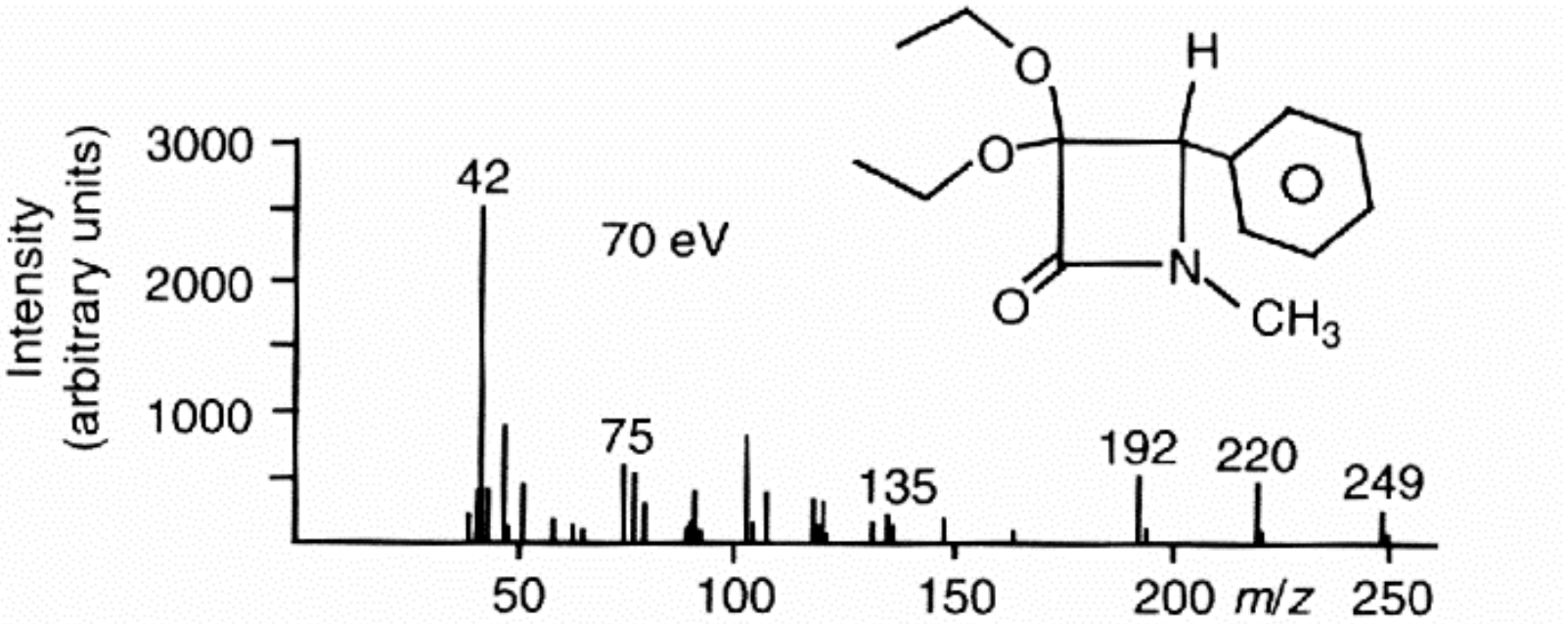
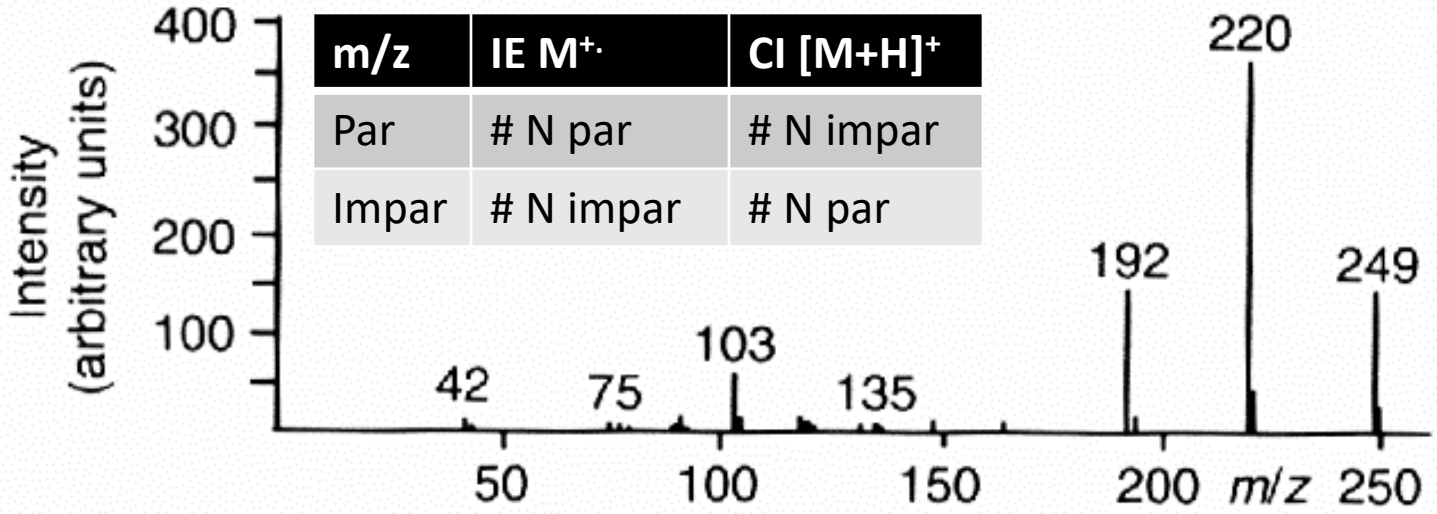
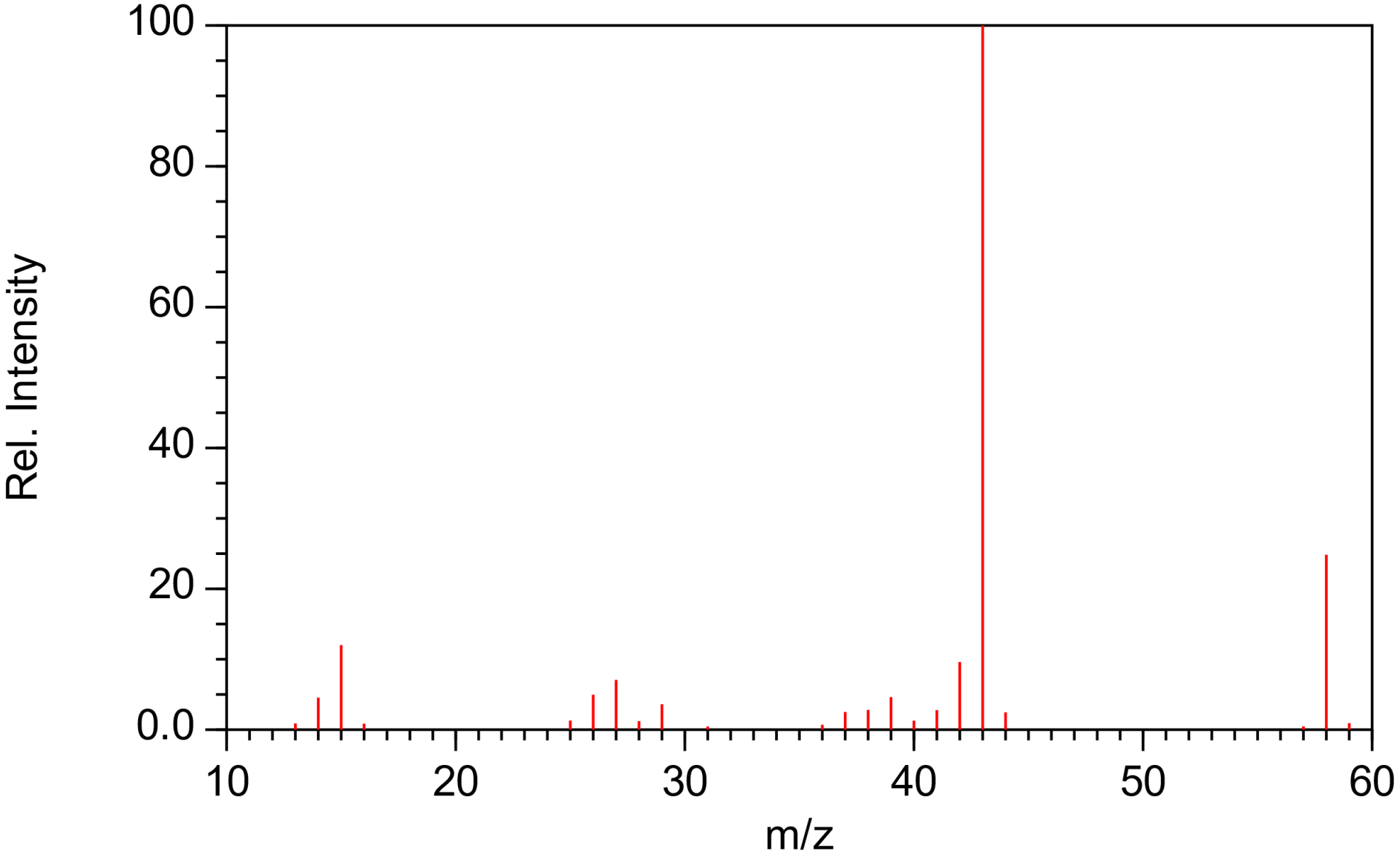




m/z	IE $M^{+\cdot}$	CI $[M+H]^+$
Par	# N par	# N impar
Impar	# N impar	# N par

Regra do Nitrogênio

Acetona



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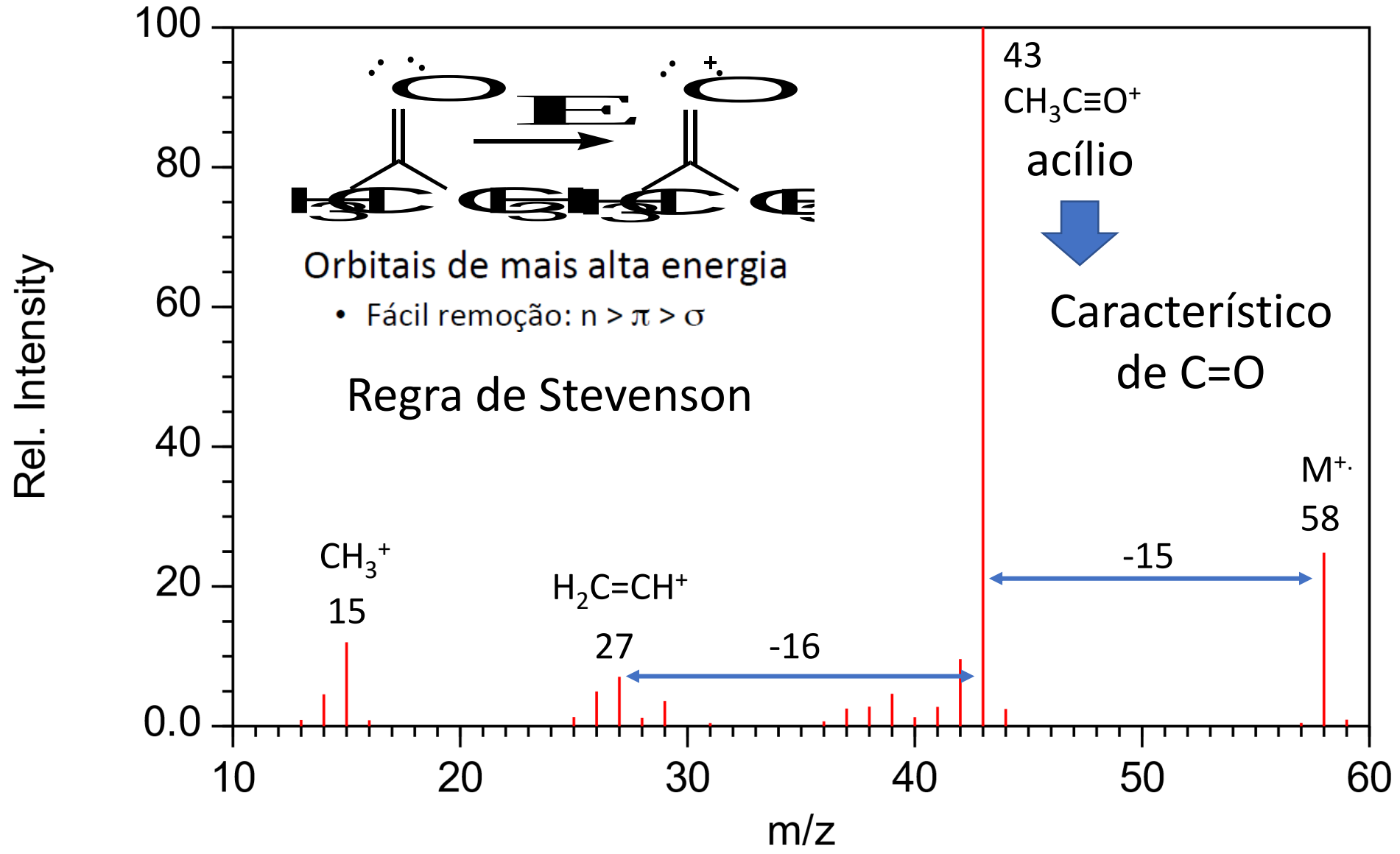
Acetona



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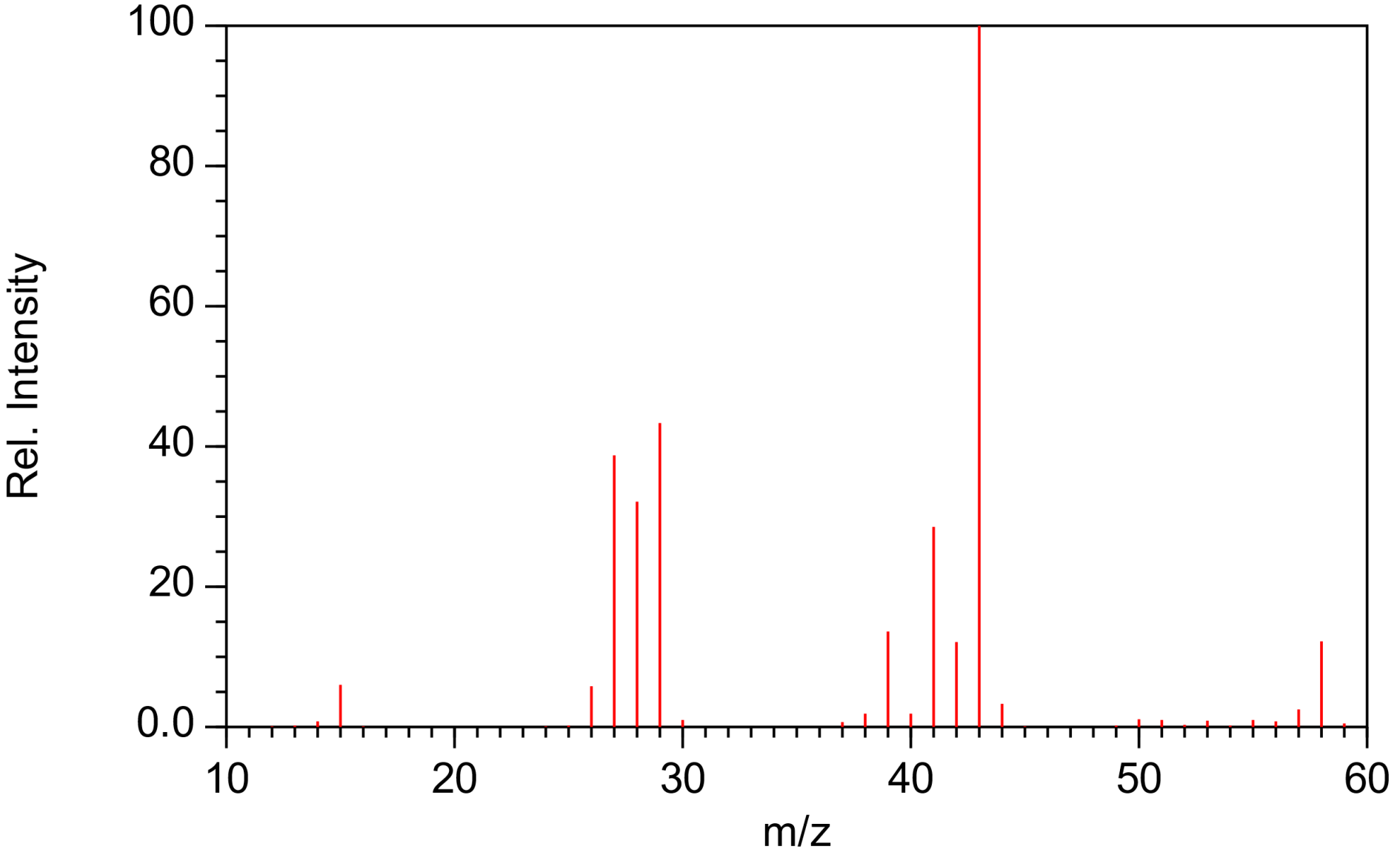
Identifique a espécie abaixo:



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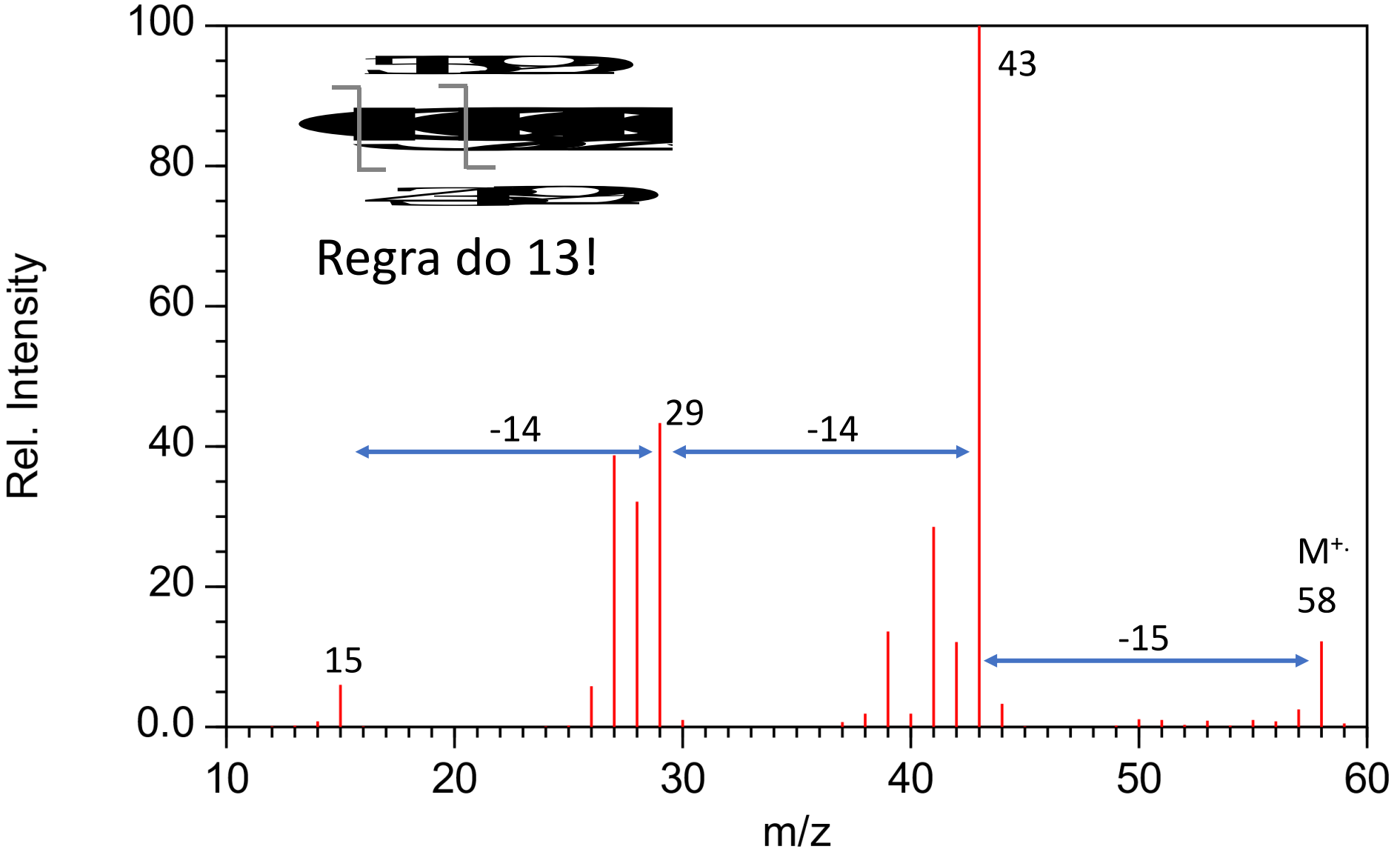

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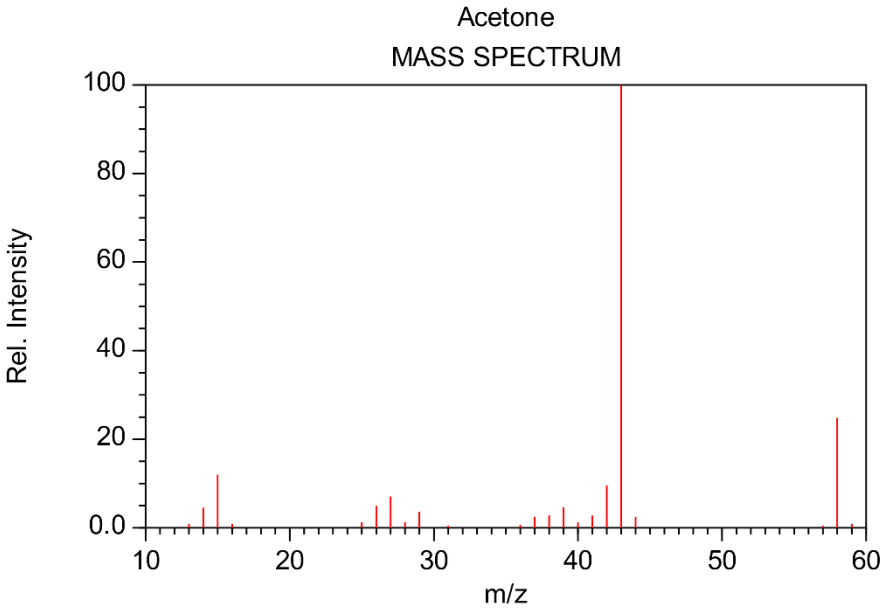
Considere todos os dados da amostra!



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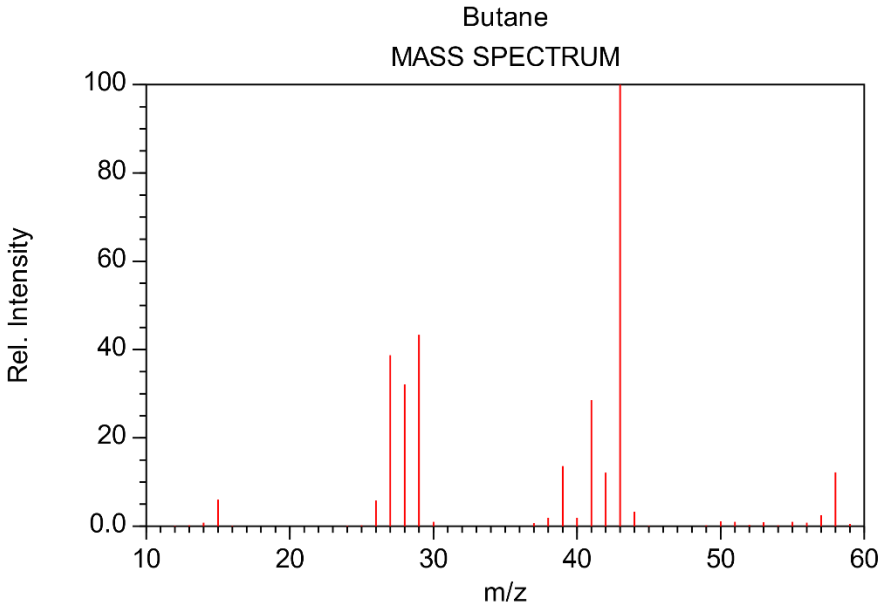

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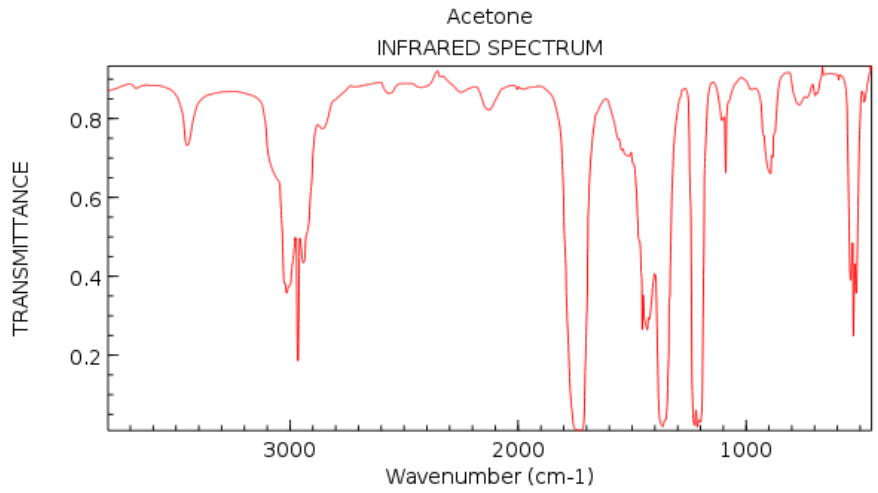

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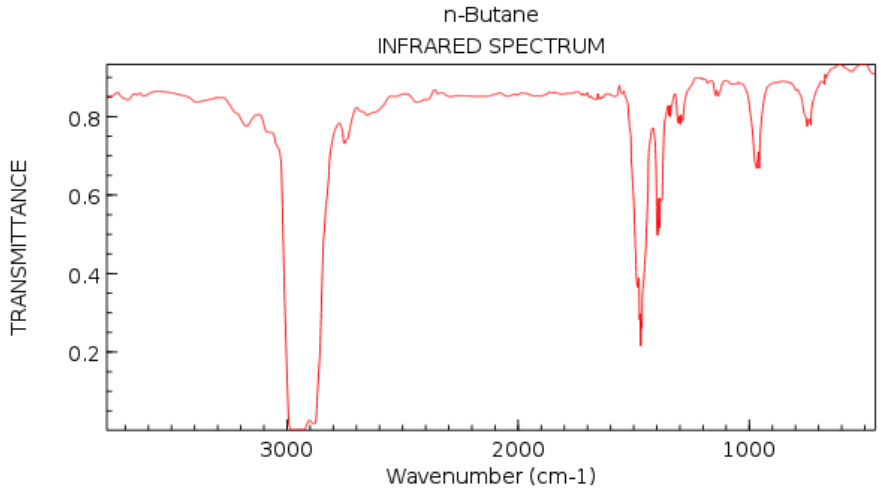

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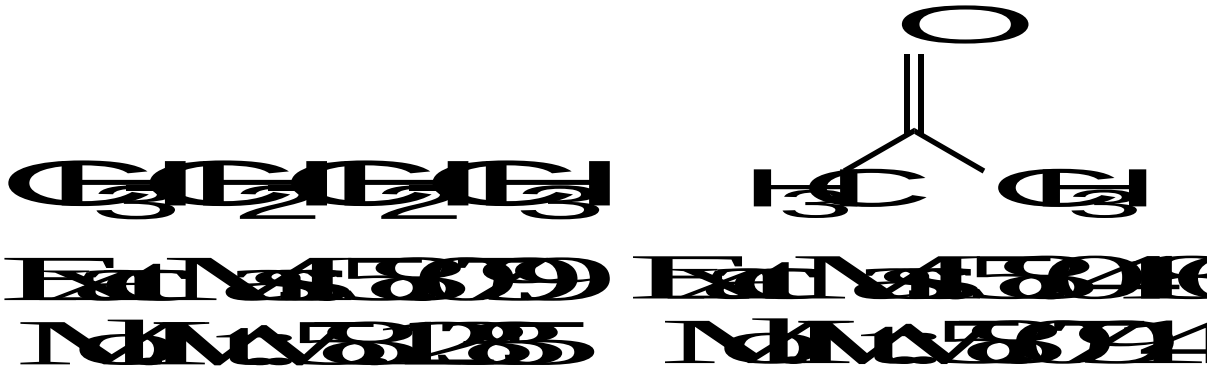
Como diferenciar Acetona n-butano por EM?

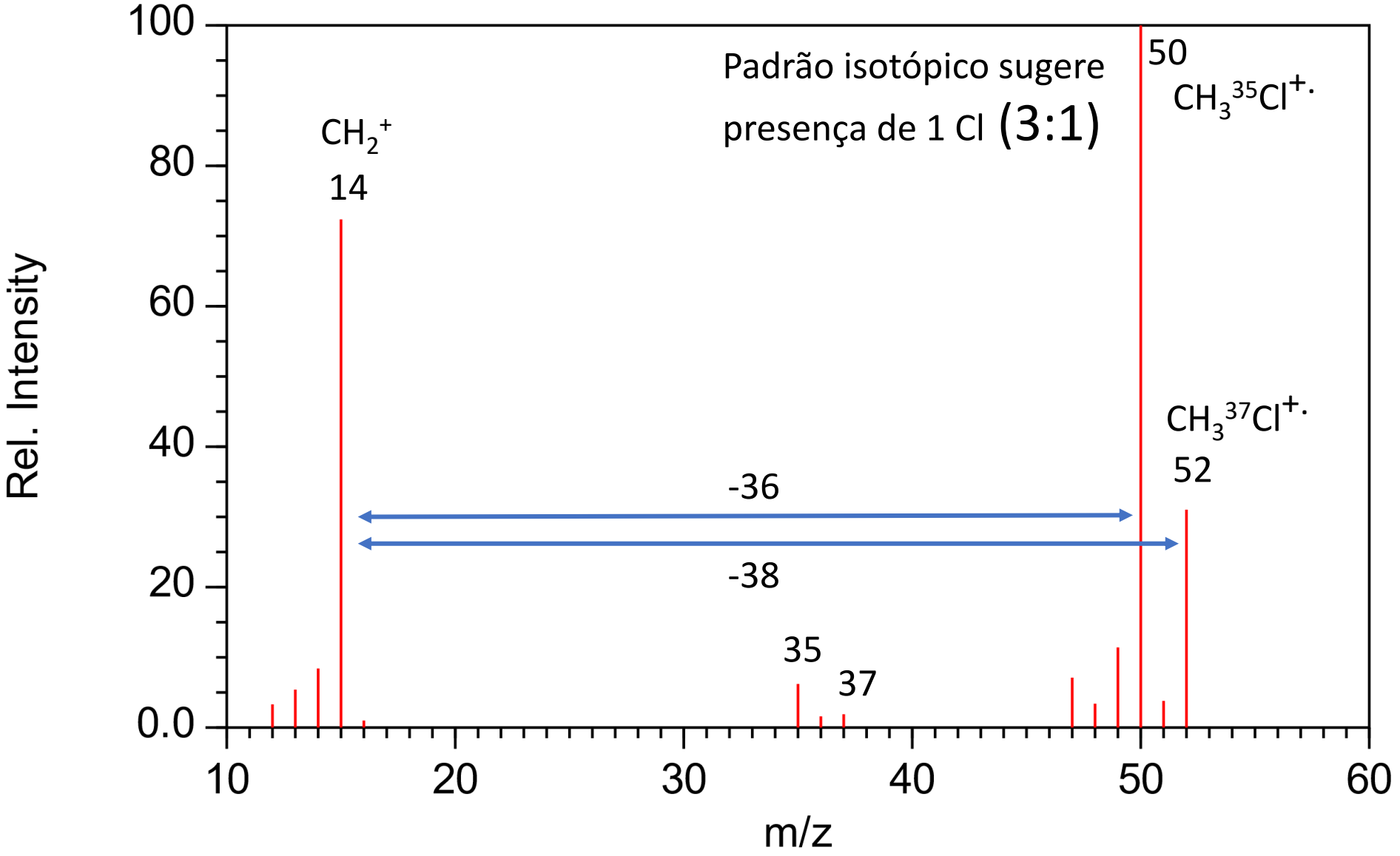


Espécie	n-butano	Acetona
Massa nominal	58	58
Massa exata	58.0799	58.04186
Massa média	58.12385	58.07914

Depende da abundancia relativa!

Alta resolução pode identificar essas espécies!

Clorometano



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Padrão Isotópico

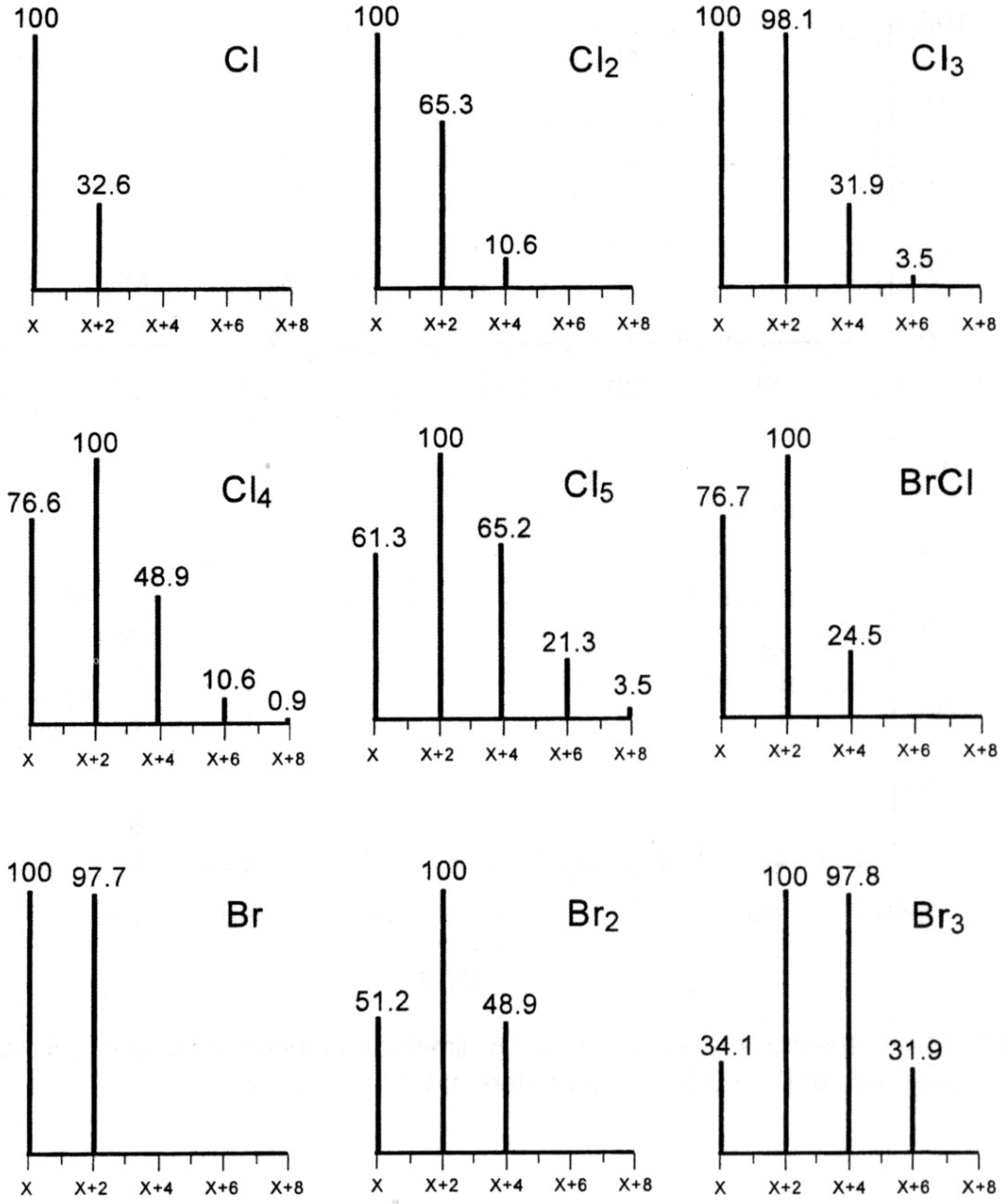


Figure 2.6. Peak intensities for some isotope clusters containing Br and Cl.

Padrões isotópicos para substancias contendo um ou mais átomos de Cl e Br

Abundância Natural

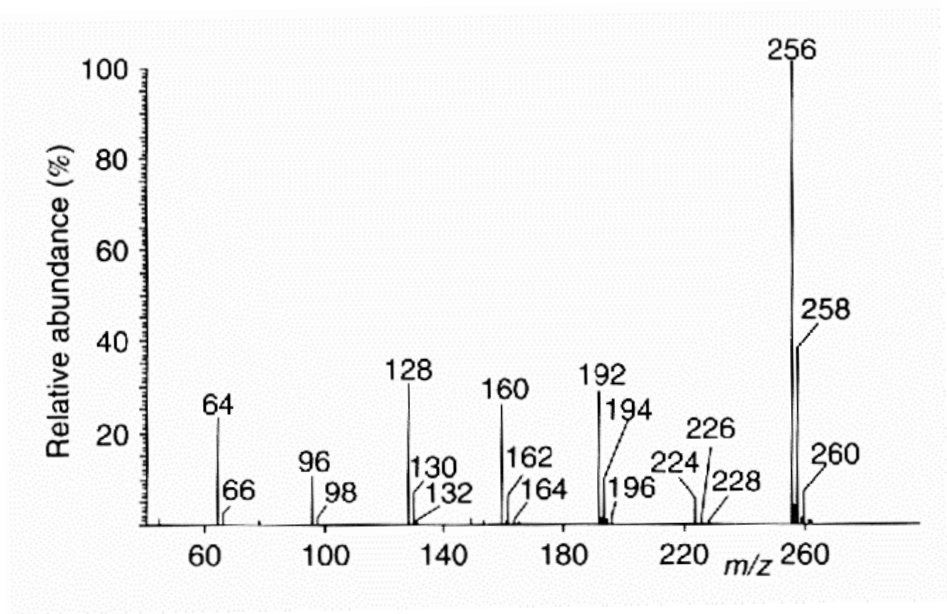
^{35}Cl - 75,41%
^{37}Cl - 24,59%

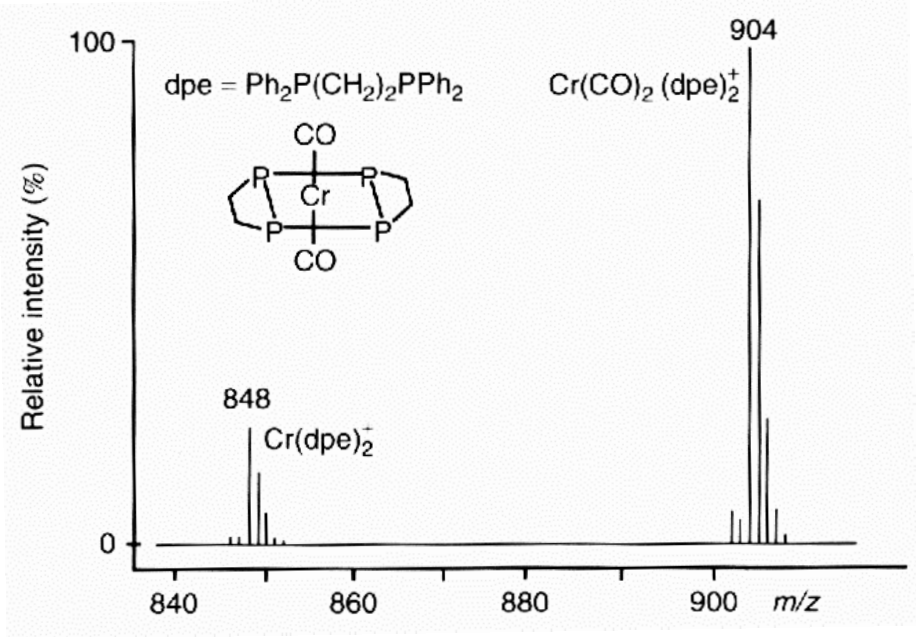
^{79}Br - 50,58%
^{81}Br - 49,42%

Espectros de massas por ionização por elétrons de sistemas inorgânicos com padrões isotópicos característicos:

a) caso do S_8 (^{32}S e ^{34}S);

b) complexo de Cr (^{50}Cr, ^{52}Cr, ^{53}Cr, ^{54}Cr)





Resumo até o momento

- Íon molecular
- Fragmentação
  - Clivagem sigma
  - Clivagem indutiva
- Regra do Nitrogênio
- Regra do 13
- Regra de Stevenson
- Massa exata
- Padrão isotópico
- Fragmentações características

Fonte de ionização:

Impacto eletrônico

Ionização Química

Tipo de amostra:

Voláteis ou gases

Baixo peso molecular