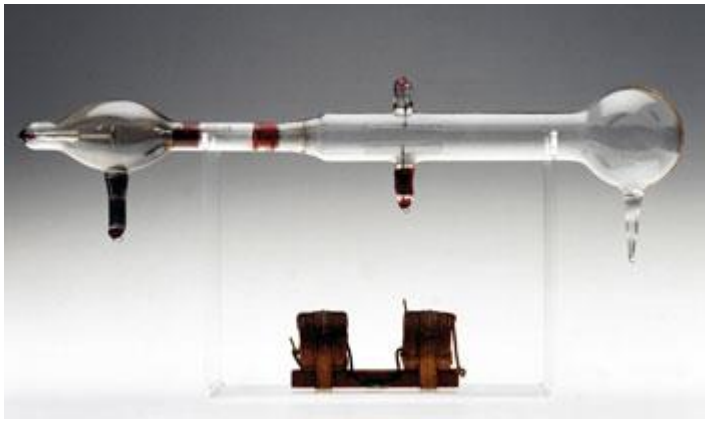
Espectrometria de massas

i) Introdução à Técnica

ii) Estudo dos Analisadores de Massa



Thomson's cathode ray tube, 1897
© Science Museum Pictorial x 2

Agilent 8800 ICP Triple Quad, 2014

ICP-MS versus IRMS

- **ICP-MS = Inductively coupled plasma Mass Spectrometry**
- Espectrometria de massas com plasma indutivamente acoplado

- **IRMS= Isotope ratio Mass Spectrometry**
- Espectrometria de massa de razão isotópica

Por que MS?

Os ultra-traços estao ausentes
ou apenas nao podem ser detectados?

Roteiro e objetivos da aula

- Recapitulação: Espectrometria de massas (MS)
- ICP-MS e IRMS: Principais características
- Visão geral dos instrumentos
- Analisadores de massa do tipo:

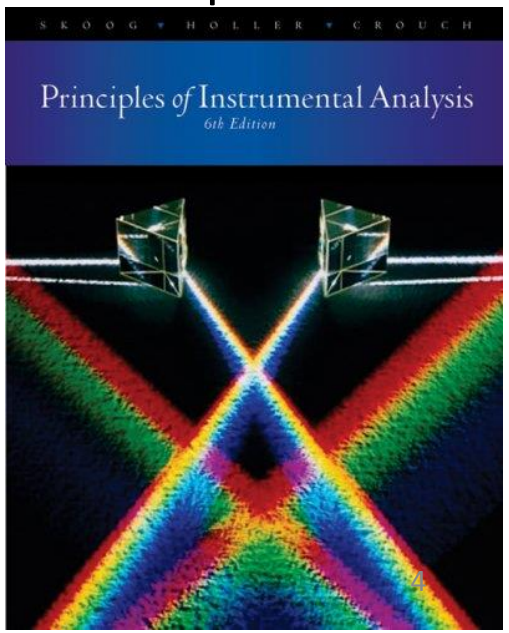
  -Quadrupolo (ICP-MS)

  -Setor magnético (IRMS AMS)

  -TOF time of flight (AMS)

Bibliografia recomendada

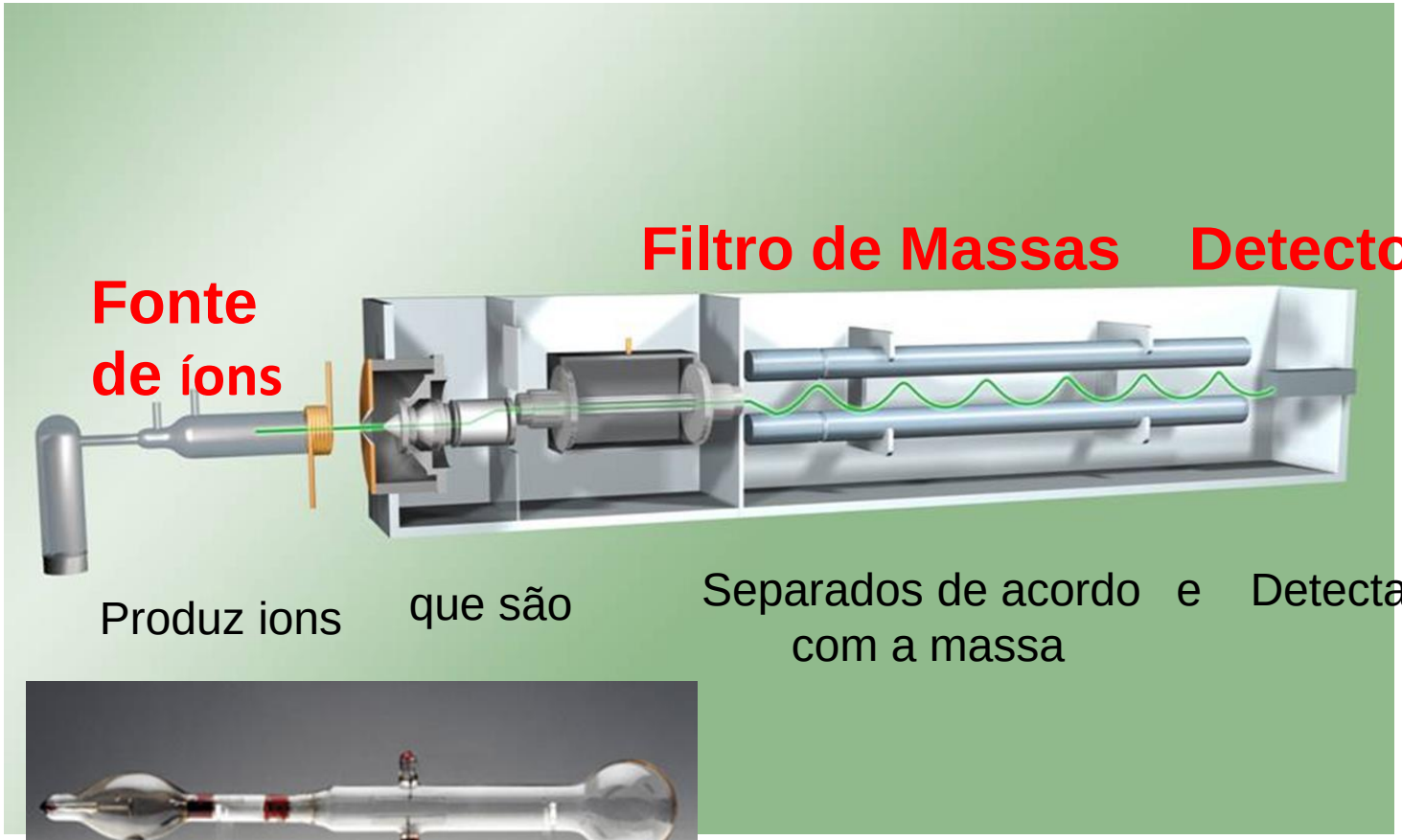
Chapter 11C

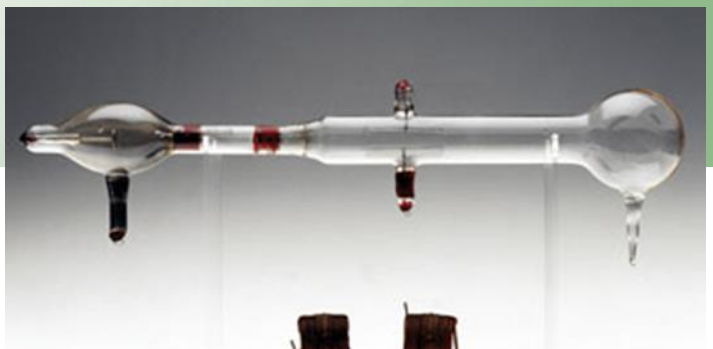


Giné-Rosias, Maria Fernanda
Espectrometria de massas com fonte de plasma. (ICP-MS). / Maria Fernanda Giné-Rosias. -- Piracicaba: CENA, 1999.
p.118 : il. (Série Didática, v.4)

Recapitulação: Espectrometria de massas (MS)

Espectrometro de massas





Principais características da ICP-MS

- Técnica de análise multielementar e isotópica
- Análises **qualitativa**, **semi-quant**. e **quantitativa**
- Medida rápida e 'simultâneas'
- Limites de detecção µg.kg^{-1} -ng.kg^{-1} (ppb-ppt)

Coloridos podem ser analisados
Por ICP-MS

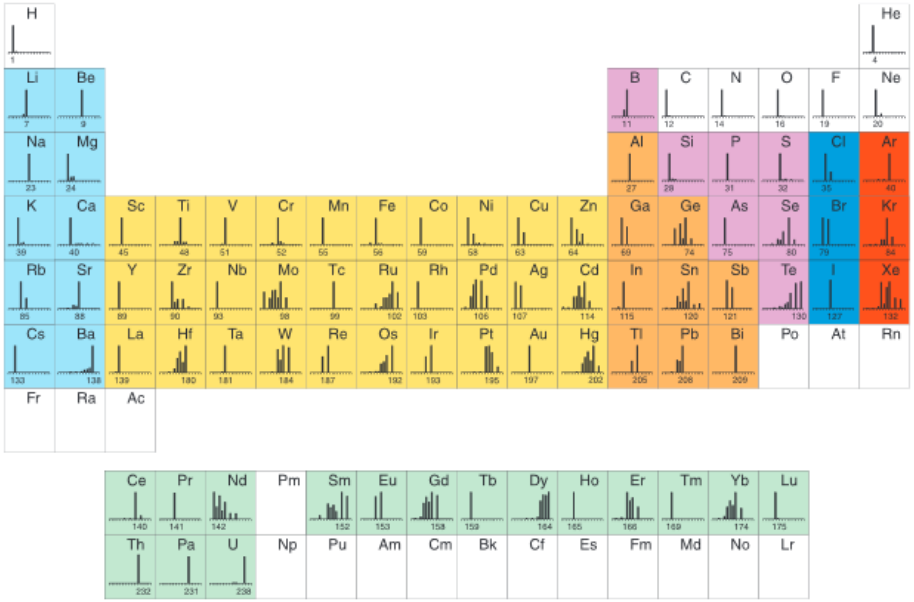
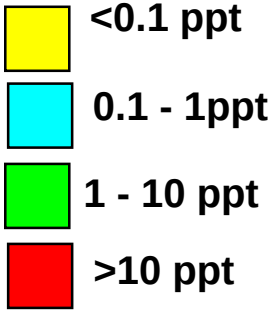
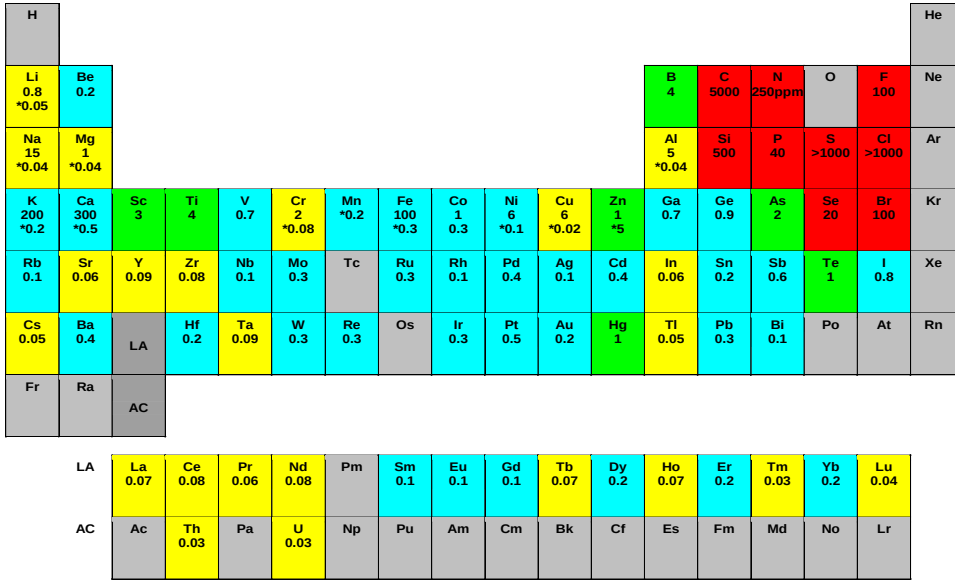


Figure 1. Elements analyzed by ICP-MS (in color).





http://www.perkinelmer.com/PDFs/Downloads/tch_icpmsthirtyminuteguide.pdf

Agilent

Principais características

- Faixa de trabalho : 9 ordens de grandeza

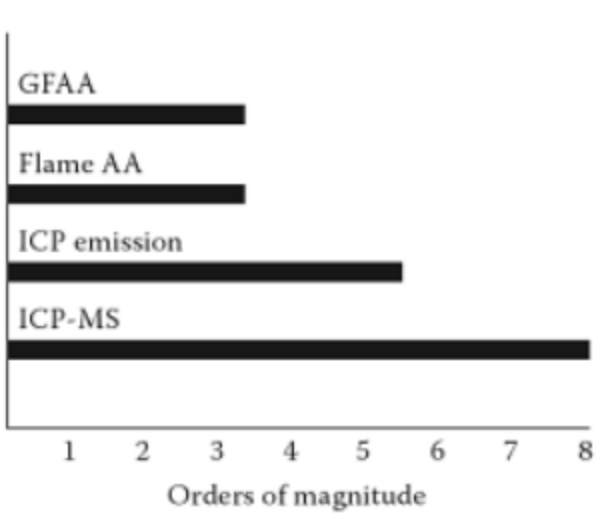
- Calibração com padrões certificados.

-Curva analítica
-padrão interno
-adição de padrão

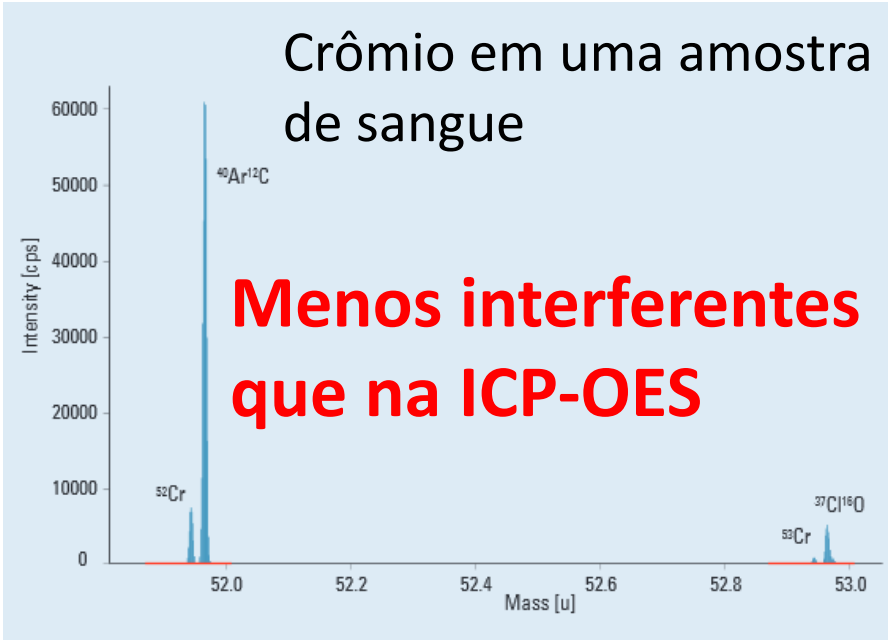
- Semi-quantitativa

-Apenas alguns padroes. Pq?

- Qual é o resultado da medida?



Practical Guide to ICP-MS: A Tutorial for Beginners, Third Edition



http://www.thermoscientific.com/content/dam/tfs/ATG/CMD/CMD%20Documents/BR-30027-Element-2-Element-XR.pdf

Principais características

- Pode ser combinada à outras técnicas:

HPLC-ICP-MS

(cromatografia)

As complexado com diferentes moléculas

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
Article
pubs.acs.org/JAFC

Application of HPLC-ICP-MS and HPLC-ESI-MS Procedures for Arsenic Speciation in Seaweeds

Yu-Jhe Hsieh[†] and Shiuh-Jen Jiang*[,†,§]

[†]Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
[§]Department of Medical Laboratory Science and Biotechnology, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

dx.doi.org/10.1021/jf204595d | *J. Agric. Food Chem.* 2012, 60, 2083–2089

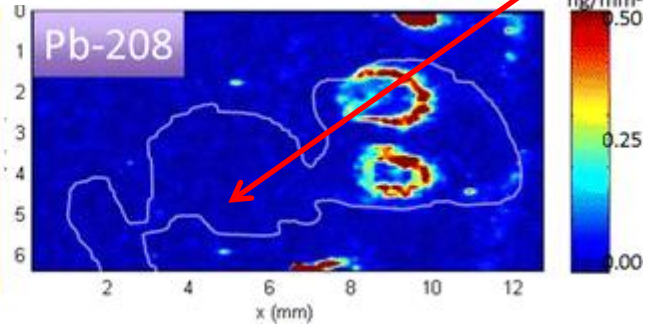
JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
Article
pubs.acs.org/JAFC

Spatial Distributions of Inorganic Elements in Honeybees (*Apis mellifera L.*) and Possible Relationships to Dietary Habits and Surrounding Environmental Pollutants

Tsing-Hai Wang, Chia-Hung Jian, Yi-Kong Hsieh, Fu-Nien Wang, and Chu-Fang Wang*

Biomedical Engineering and Environment Sciences, National Tsing Hua University, Taiwan

dx.doi.org/10.1021/jf400695w | *J. Agric. Food Chem.* 2013, 61, 5009–5015



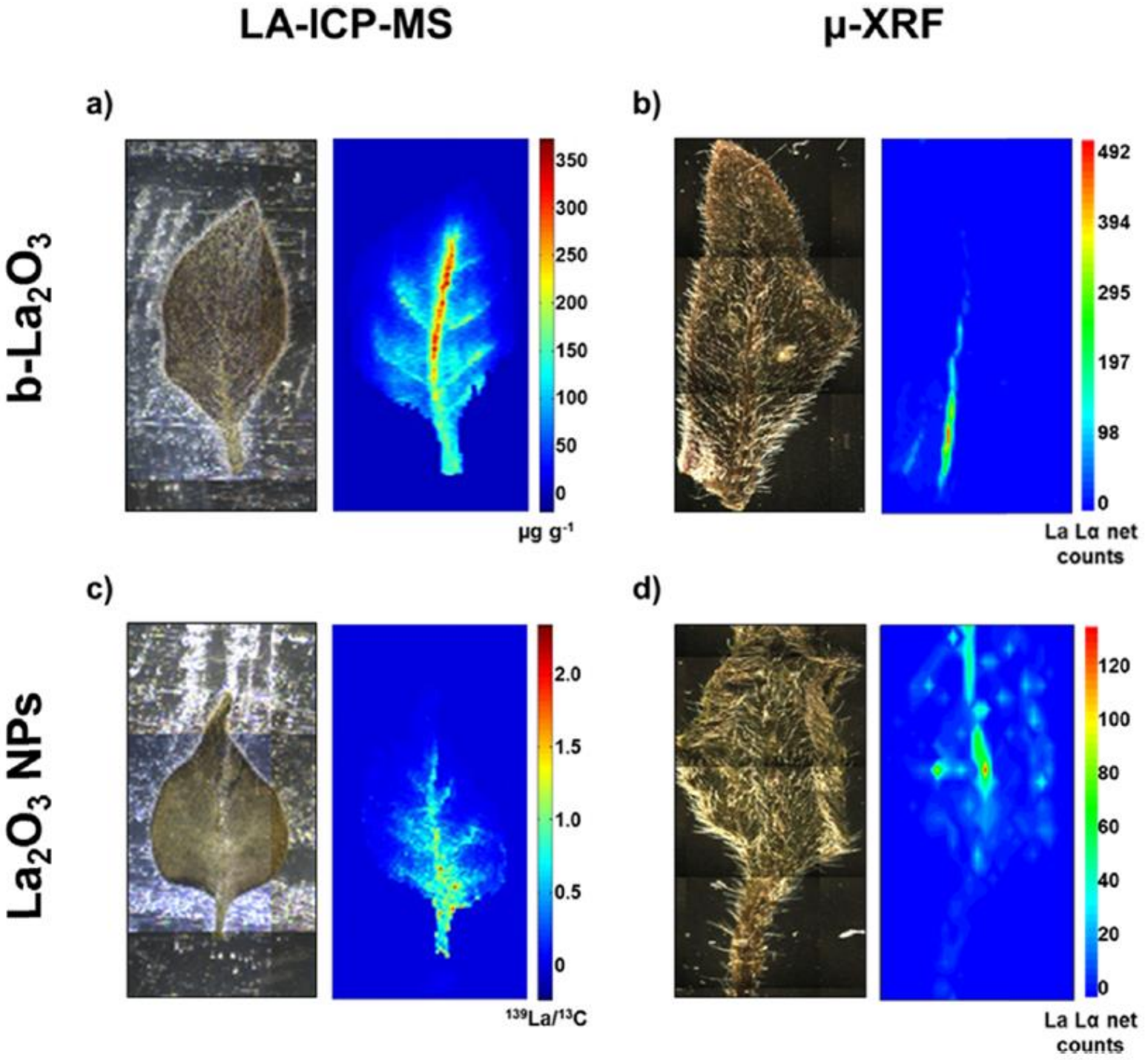
Corpo da abelha!

LA-ICP-MS

(ablação por laser)

Mapas-distribuição espacial elementar

- Existem aplicações mais simples?


LA-ICP-MS
μ-XRF
a)
b)
c)
d)
b-La2O3
La2O3 NPs
350
300
250
200
150
100
50
0
μg g-1
492
394
295
197
98
0
La Lα net counts
2.0
1.5
1.0
0.5
0
139La/13C
120
100
80
60
40
20
0
La Lα net counts

Principais características

- **Vantagens**
  - Baixíssimos limites de deteção
  - Quase todos os elementos da tabela periódica
  - Ampla faixa de trabalho (9 ordens)
  - Espectro mais simples que o da ICP-OES
  - Pequeno volume amostra
  - Informação isotópica

  (^{129}I Fukushima)
  - Metodos de calibracao flexíveis

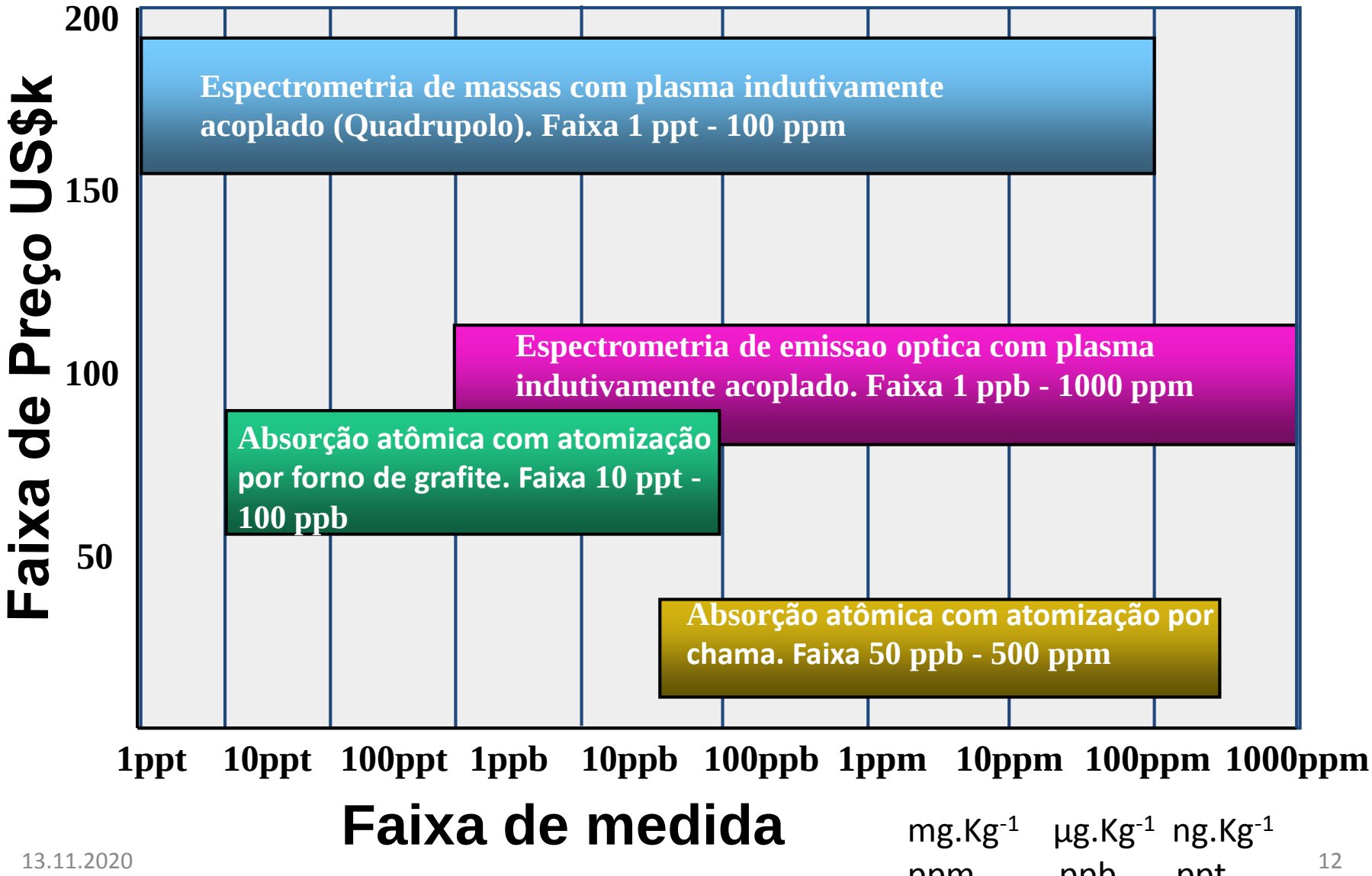
- **Desvantagens**
  - Efeitos de matriz
  - Alto custo de aquisição e operação
  - Requer um analista altamente treinado

2962 m

https://pt.wikipedia.org/wiki/Zugspitze

Principais características

Comparação preço x performance



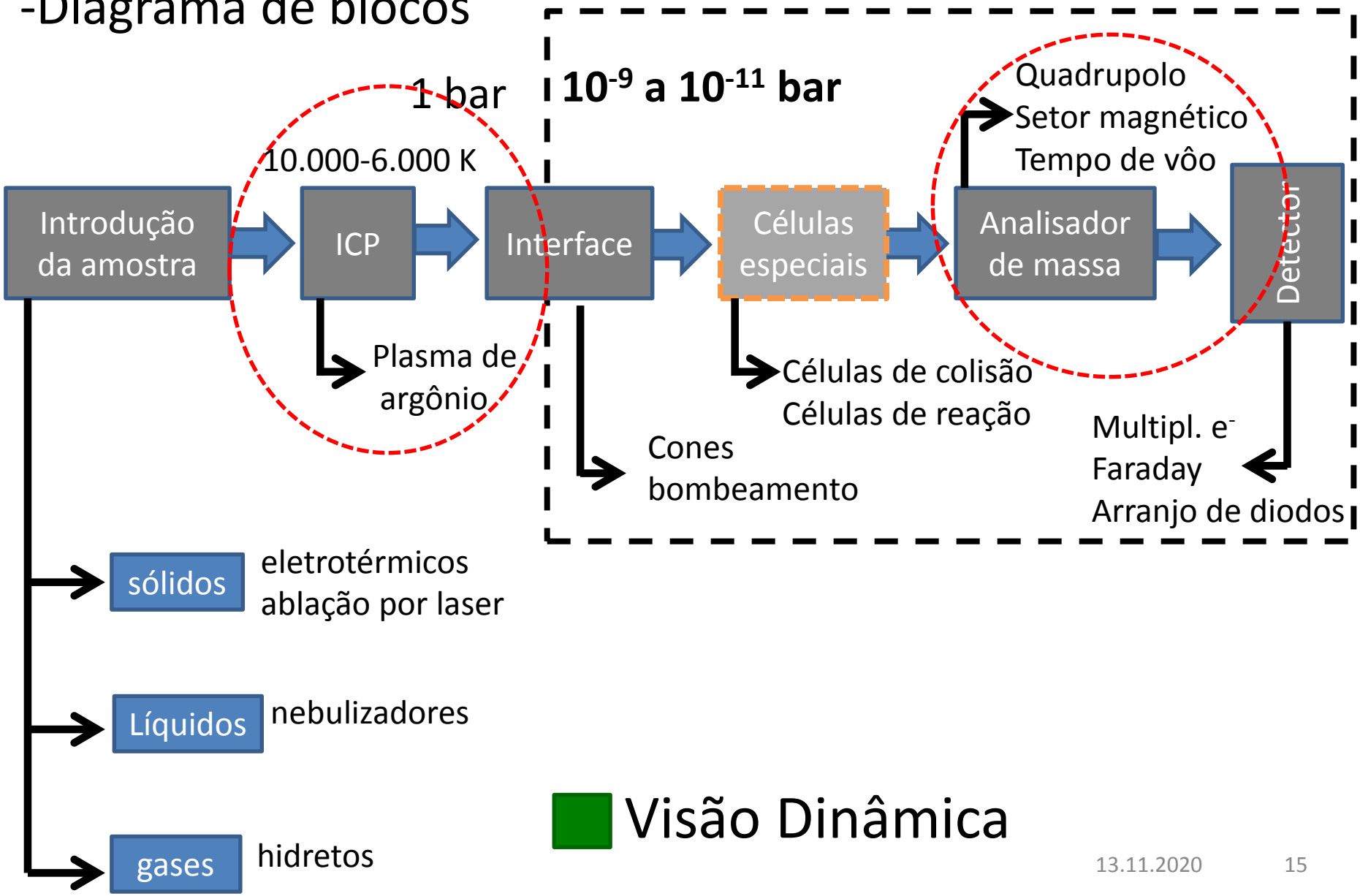
mg.Kg^{-1} ppm µg.Kg^{-1} ppb ng.Kg^{-1} ppt

Visão Geral dos Equipamentos

ICP-MS

Visão Geral do Equipamento

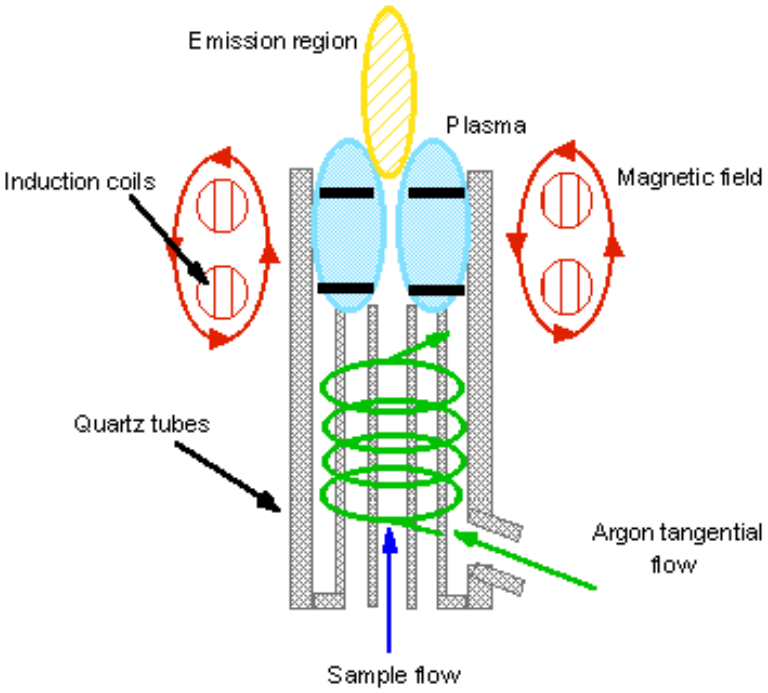
-Diagrama de blocos

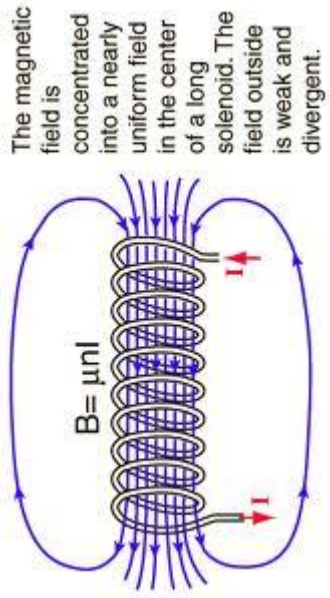


Visão Dinâmica

Visão Geral do Equipamento

-ICP: Plasma ***Indutivamente*** Acoplado

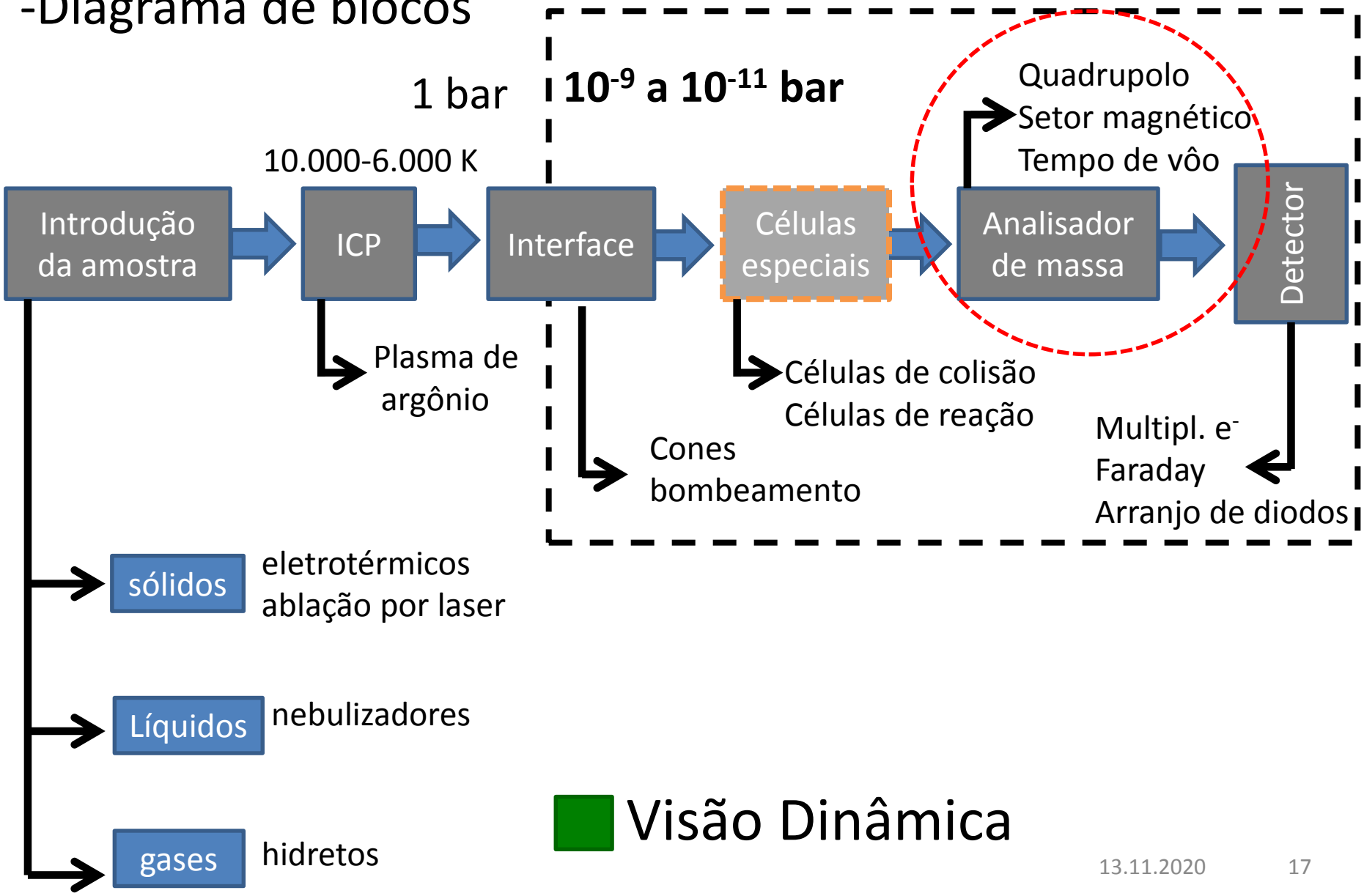




-ICP: Radio Frequência de Alta Potência

Visão Geral do Equipamento

-Diagrama de blocos

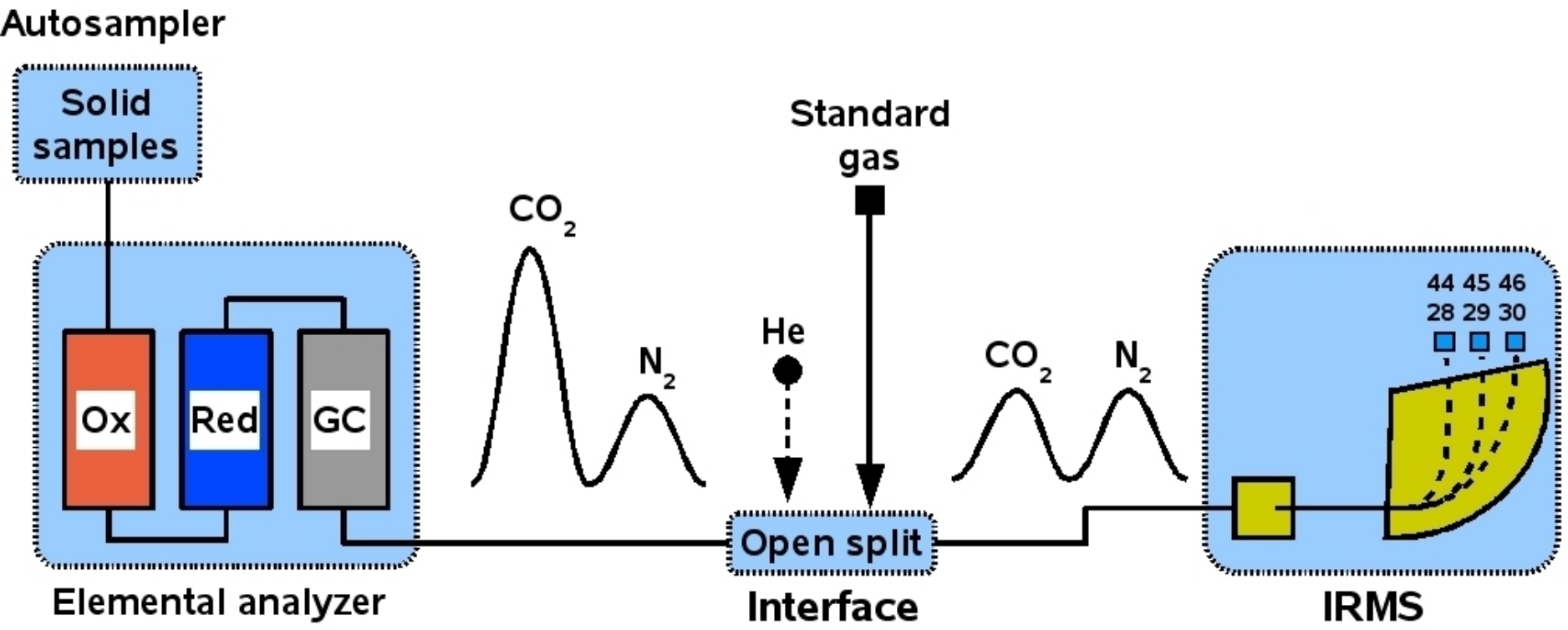


Visão Dinâmica


7500ce ICP-MS
Agilent Technologies

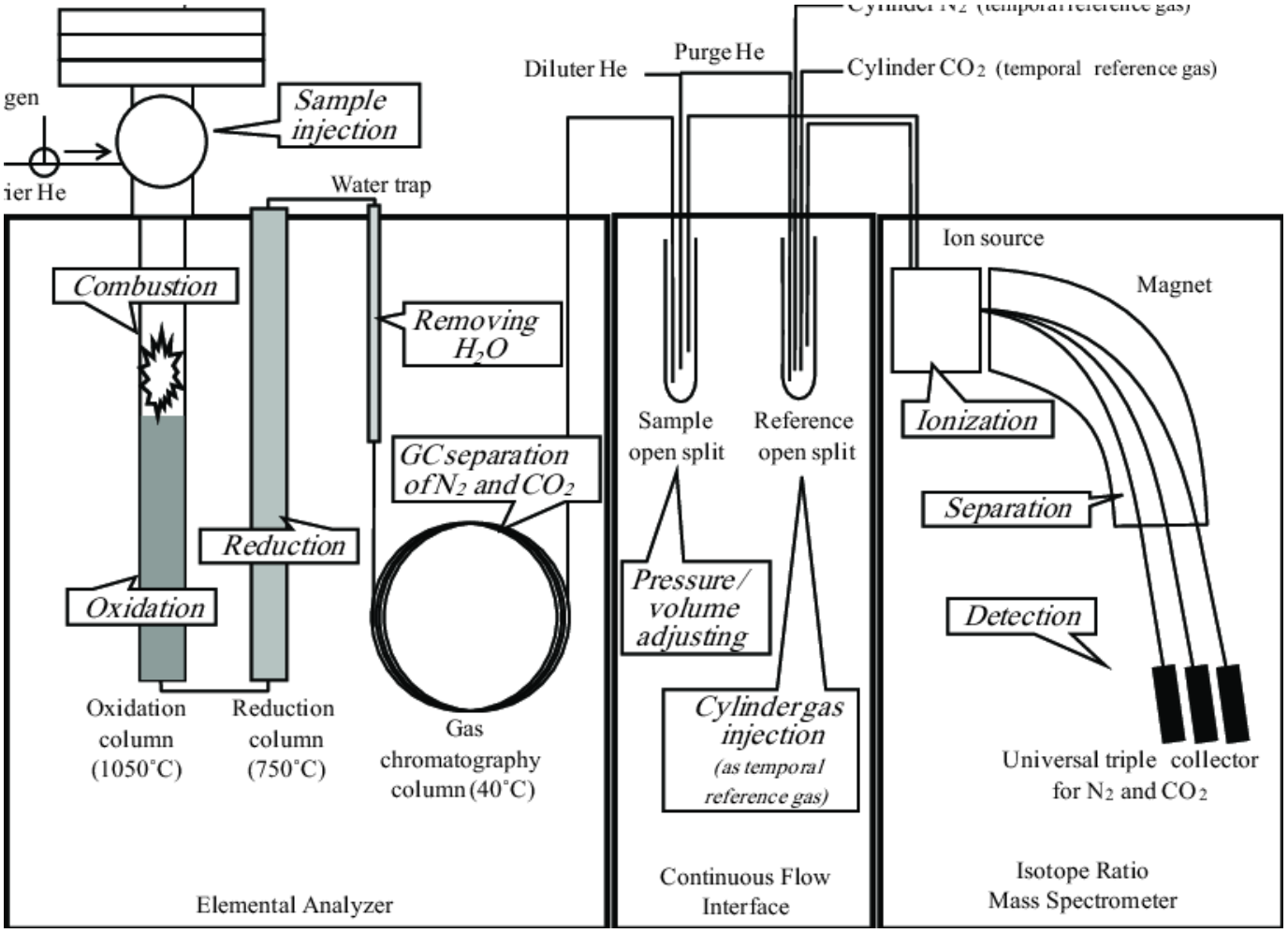
IR-MS

Visão Geral do Equipamento



https://www.bayceer.uni-bayreuth.de/ibg/en/ausstattung/geraet/geraet_detail.php?id_obj=65905

Visão Geral do Equipamento

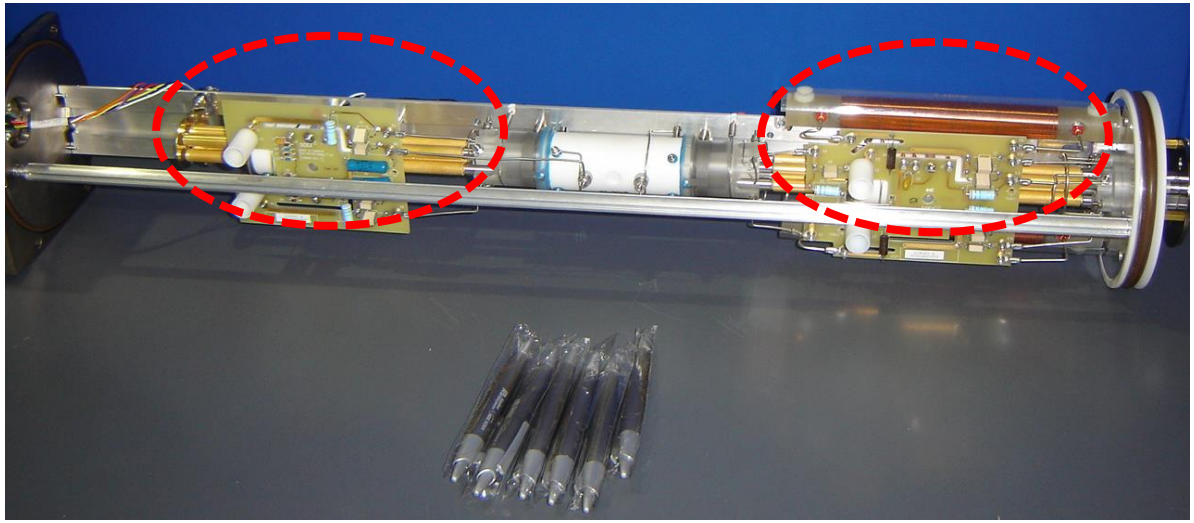


https://www.researchgate.net/publication/285816977_Ultra-sensitive_elemental_analyzerisotope_ratio_mass_spectrometer_for_stable_nitrogen_and_carbon_isotope_analyses/figures?lo=1

Analisadores de massa

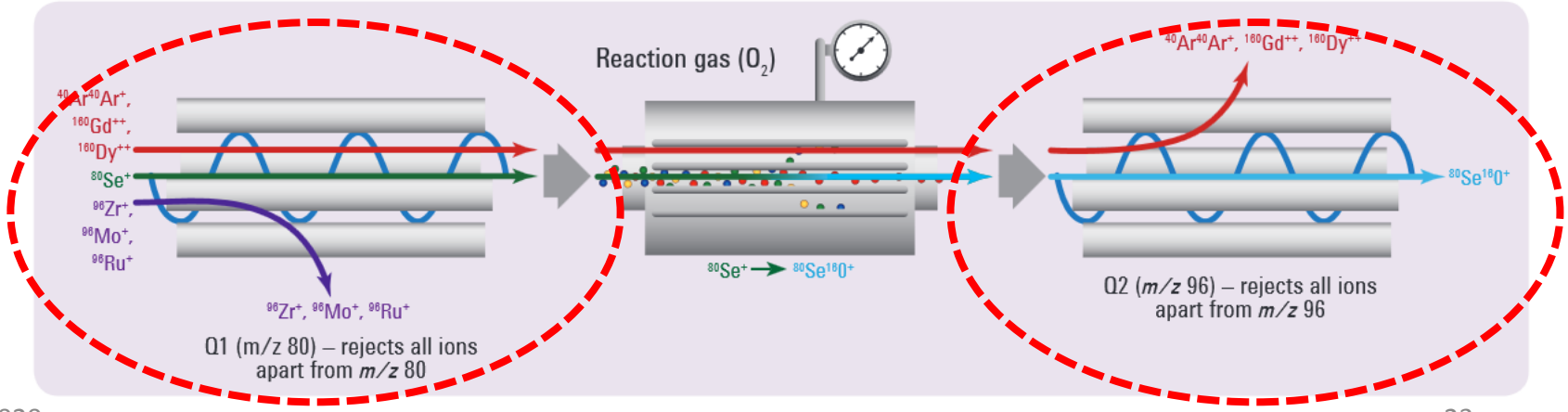
Quadrupolo

- Filtro: uma massa de cada vez
- varredura m/Z
- Tempo: ms
- Resolução: m/Δm~300 ou ± 1 u



pessoal, RASBQ 2007

B: ICP-QQQ. Q1 allows only ions at m/z 80 to pass to the cell – all other ions are rejected. $^{80}Se^{+}$ is converted to $^{80}Se^{16}O^{+}$ in the cell with O_2 reaction gas. Q2 measures SeO^{+} at m/z 96. Zr, Mo and Ru cannot interfere since they were rejected by Q1.

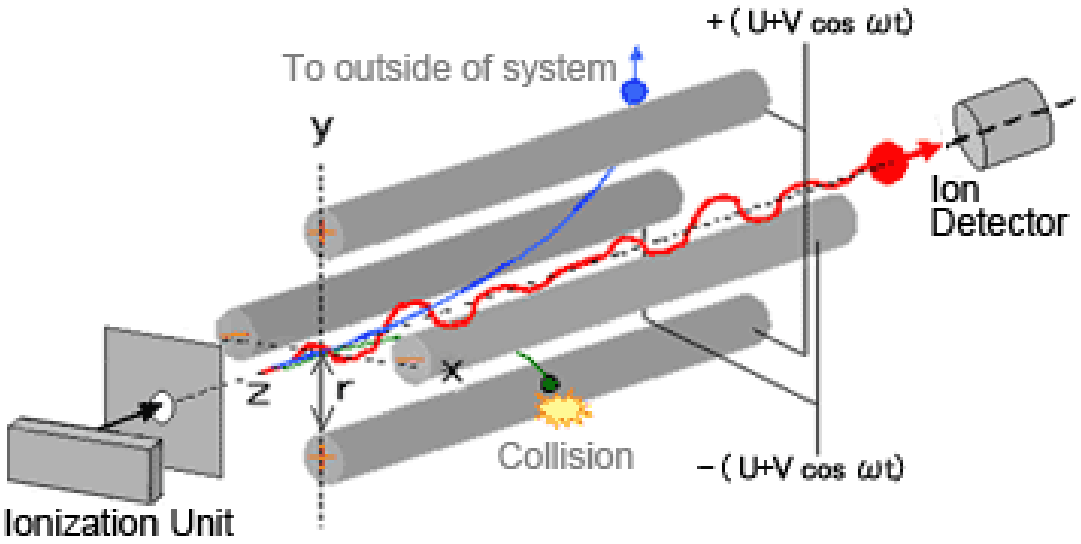


http://www.chem.agilent.com/Library/brochures/5991-0079EN_8800_ICPQQQ_Brochure.pdf

Quadrupolo

- Como funciona o quadrupolo?
- Corrente contínua (CC)/radio frequencia (RF)

- Momento p=mv



http://www.shimadzu.com/an/lcms/support/intro/lib/lctalk/61/61intro.html

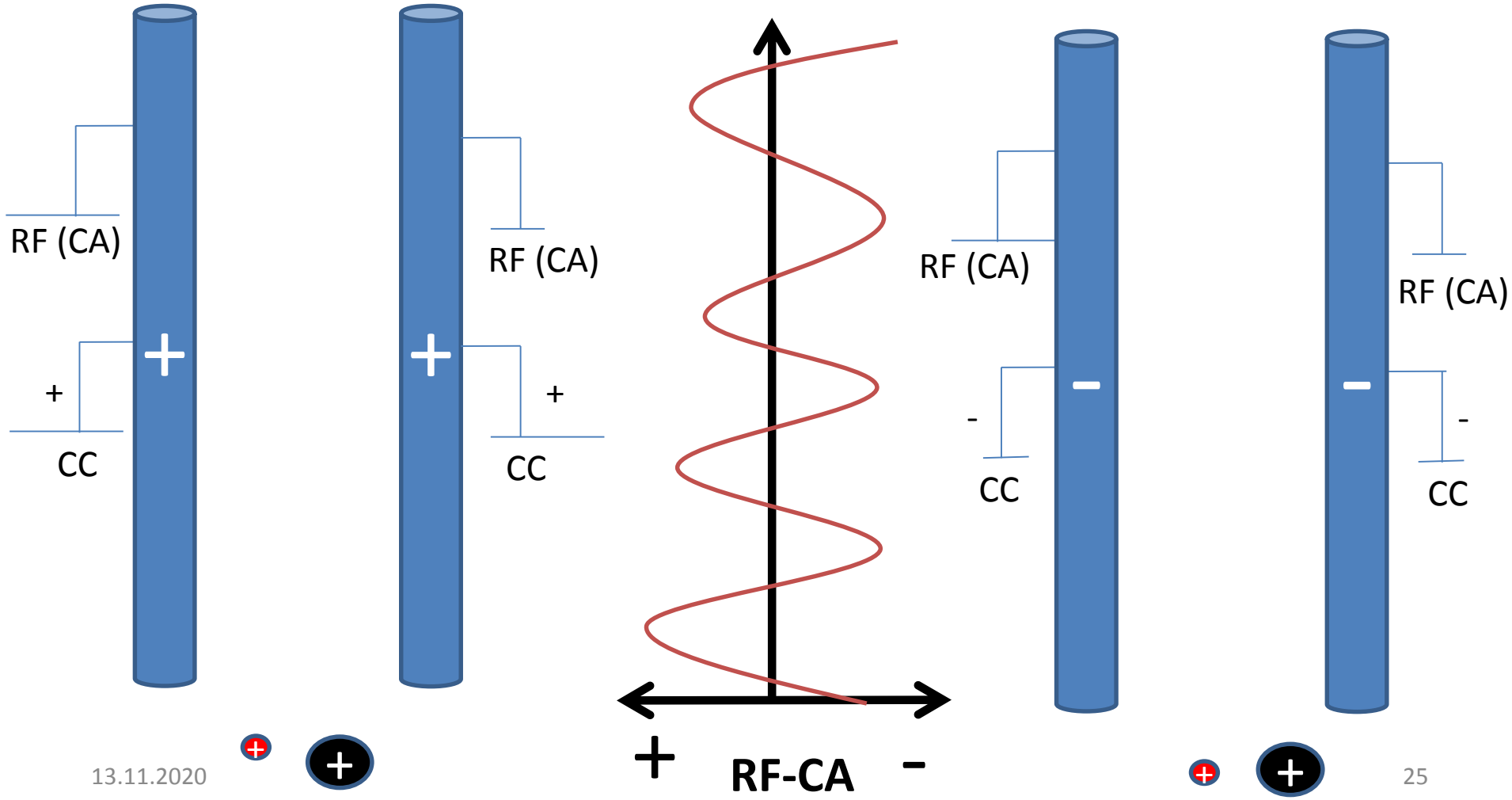
http://mlb-s1-p.mlstatic.com/vendo-mercedes-1113-bau-ano-73-pneus-zerado-13713-MLB4446134267_062013-F.jpg

http://origin.fstatic.com.br/240x180/moto-honda-cg-125-1978_28b7938f.jpg

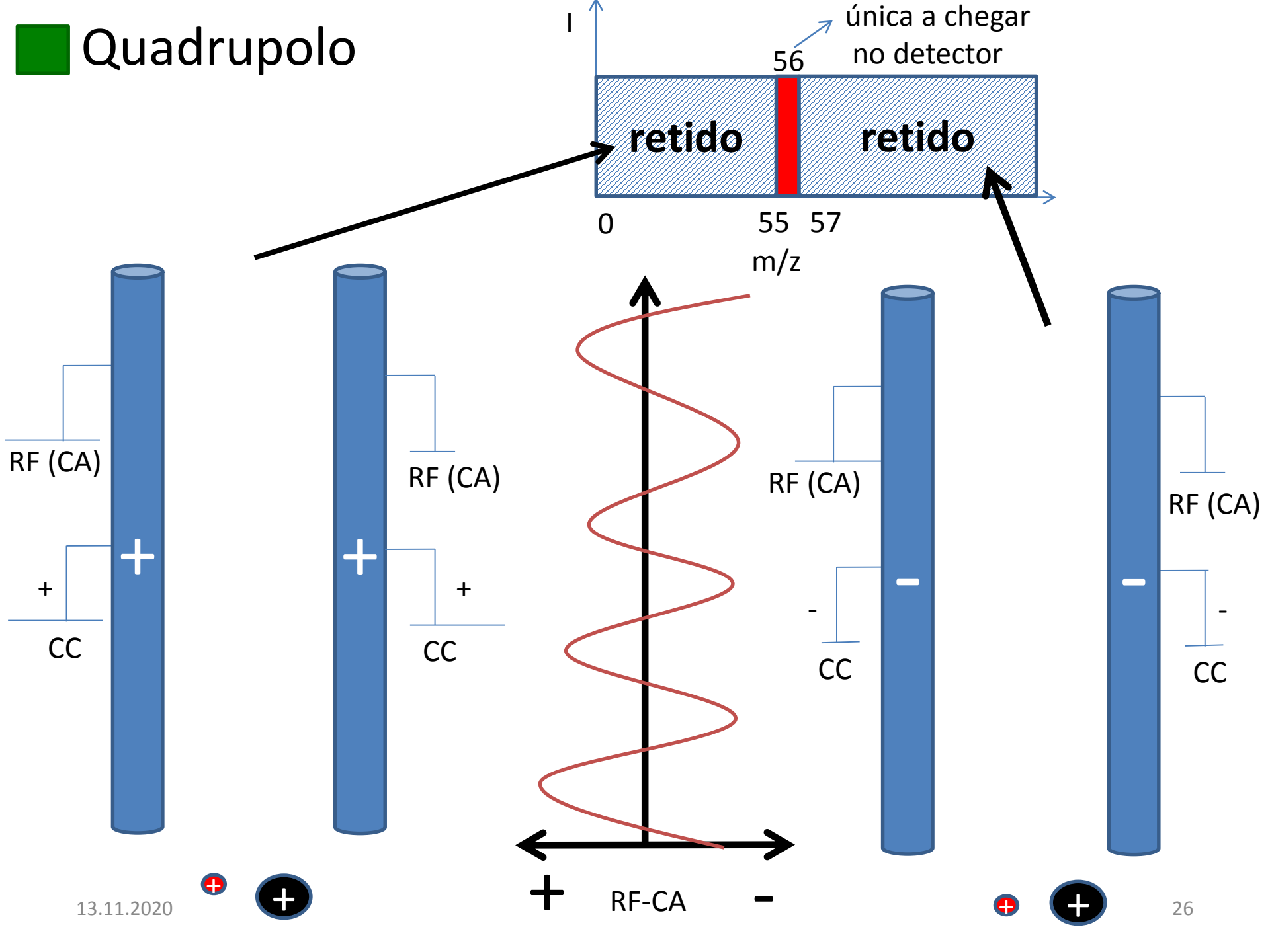
Quadrupolo

-Filtro de massas maiores (m_h)
-Apenas massas $m_h > m_l$ passam
-ex: todas as massas < 56 m/z ficam retidas

-Filtro de massas menores (m_l)
-Apenas massas $m_l < m_h$ passam
-ex: todas as massas > 56 m/z ficam retidas



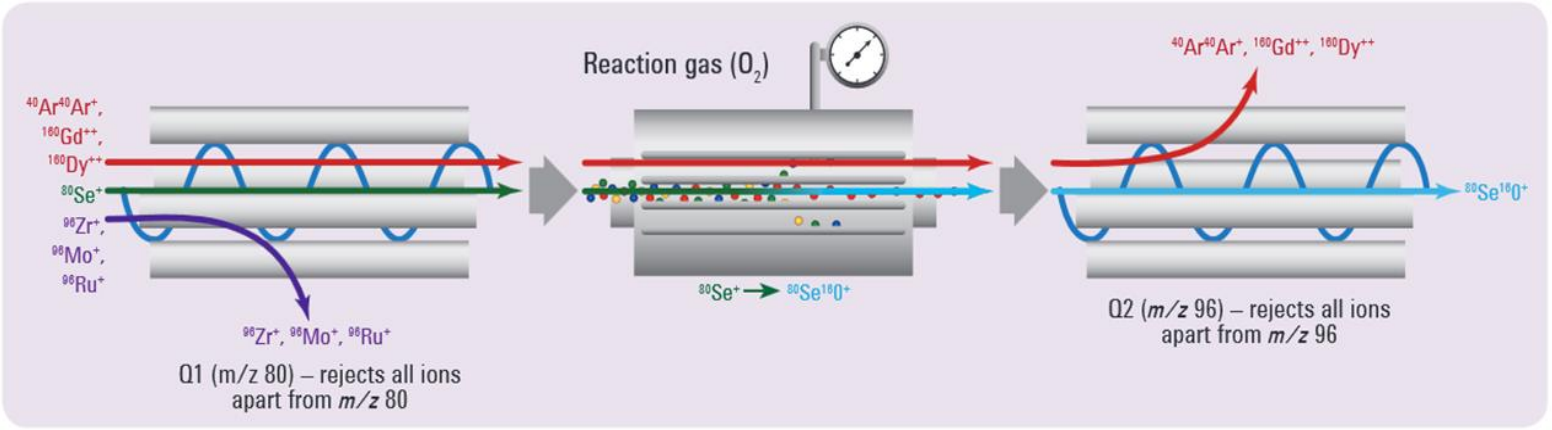
Quadrupolo

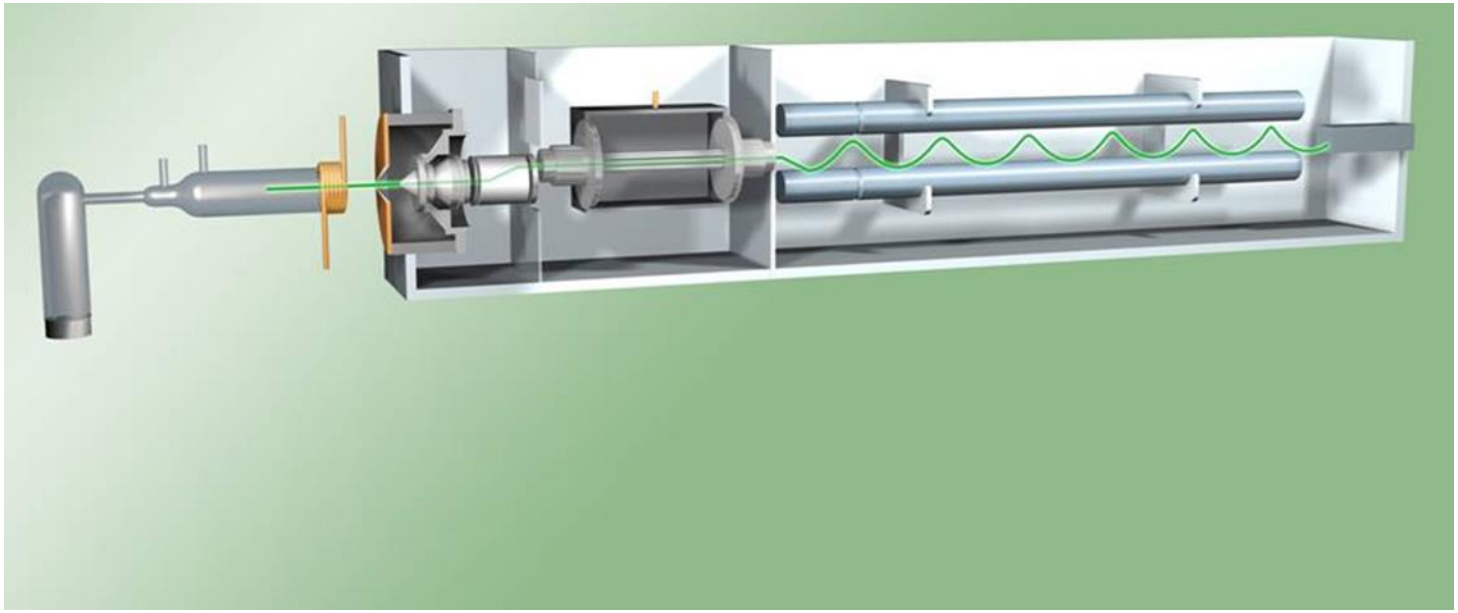

I
única a chegar no detector
56
retido
retido
0
55
57
m/z
RF (CA)
+
CC
RF (CA)
+
CC
RF (CA)
-
CC
RF (CA)
-
CC
+
RF-CA
-

Quadrupolo

-Duas configurações mais comuns

B: ICP-QQQ. Q1 allows only ions at m/z 80 to pass to the cell – all other ions are rejected. $^{80}Se^+$ is converted to $^{80}Se^{16}O^+$ in the cell with O_2 reaction gas. Q2 measures SeO^+ at m/z 96. Zr, Mo and Ru cannot interfere since they were rejected by Q1.



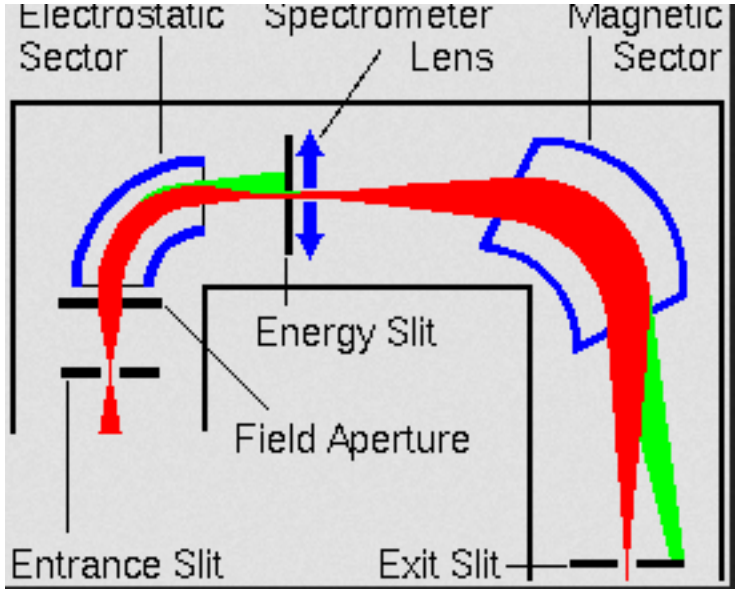


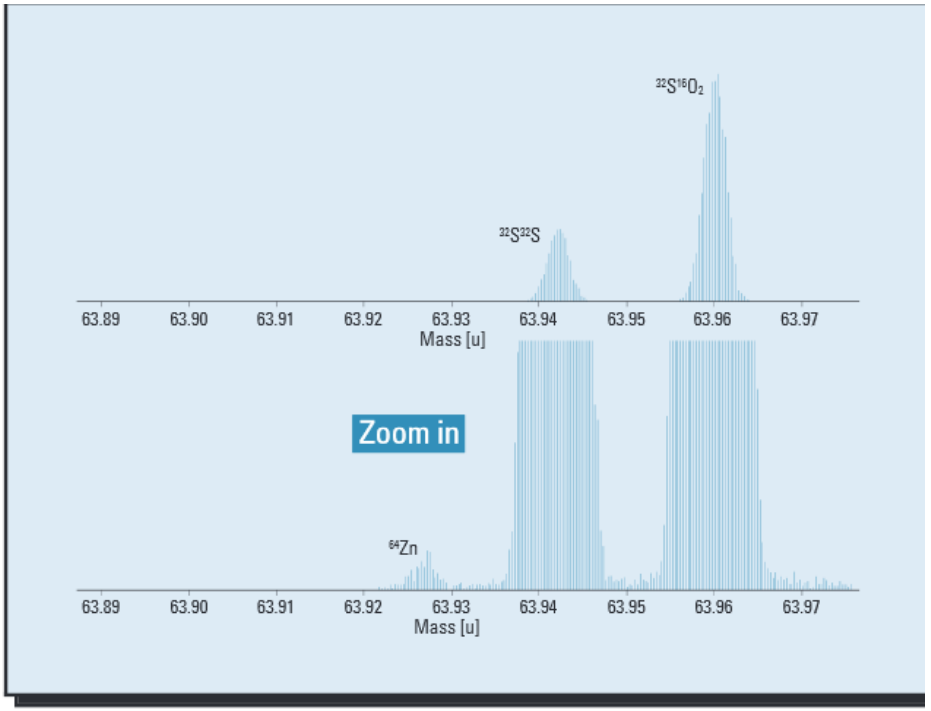
Setor Magnético

- Resolução: m/Δm~10.000 ou ± 0.007 u
- Existem várias configurações
- ex:

i) o setor eletrostático colima e ajusta a KE (energia cinética)

ii) o magnético filtra.





Zinc in H_2SO_4 (10 % w/w), High Resolution

http://www.thermoscientific.com/content/dam/tfs/ATG/CMD/CMD%20Documents/BR-30027-Element-2-Element-XR.pdf

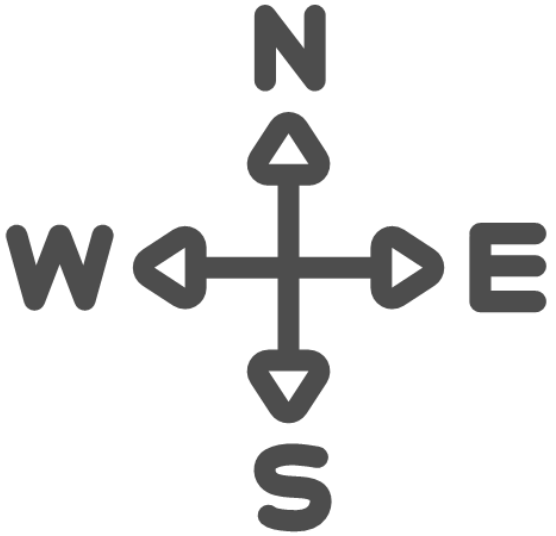

m/z
1x
m/z
10x

Video

https://www.youtube.com/watch?v=-xlpK31bjYA

Videos for discussions

Application of Stable Isotope Ratio Analysis



Caso 1

https://www.youtube.com/watch?v=nz9KUs3F1Xw

Caso 2

https://www.youtube.com/watch?v=hiHEalXlWo4