

CEN 0260

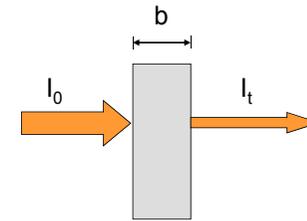
Métodos instrumentais de análise química

Espectrometria de absorção atômica

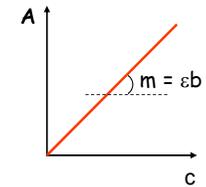
Fábio R. P. Rocha

(frprocha@cena.usp.br)

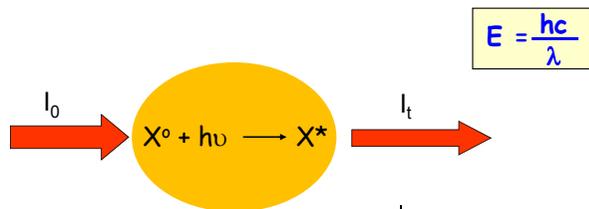
Espectrofotometria de absorção molecular



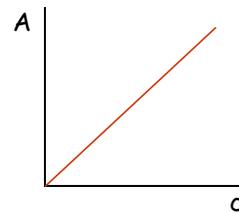
⇒ Lei de Beer: $A = \epsilon bc$



Espectrofotometria de absorção atômica



$A = \log (I_0/I_t) = abc$



Queimador

Nebulizador

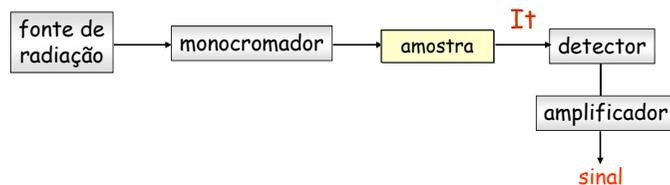
Espectrometria de absorção atômica

Técnica analítica que se baseia na medida da absorção de radiação das regiões visível ou ultravioleta do espectro eletromagnético por átomos gasosos no estado fundamental

Table of Elements for Atomic Absorption

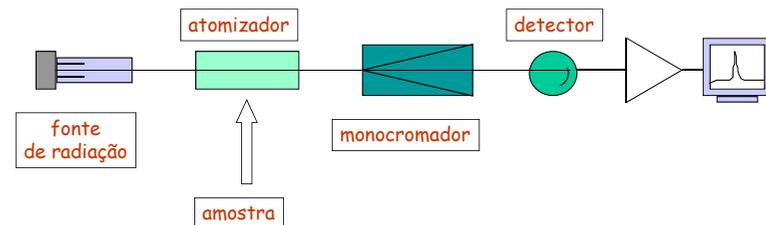
■ Red box: hollow cathode lamps of these elements are available from Spectra-Physics
 ■ Blue box: hollow cathode lamps of these elements are available from Fluoro-Lumac
 ■ Green box: hollow cathode lamps of these elements are available from Jandel-Edwards

Espectrofotômetros UV-vis

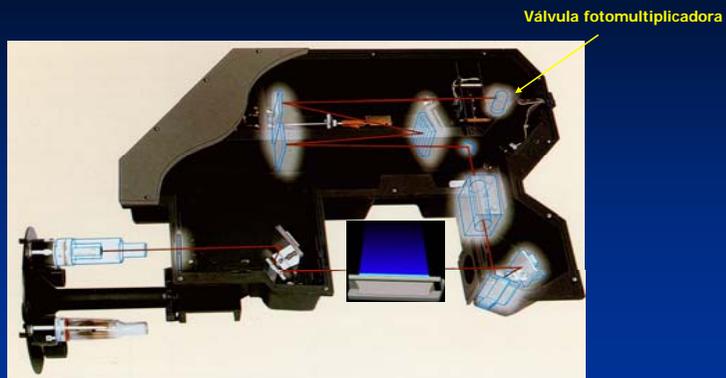


$$A = \log(I_0/I_t)$$

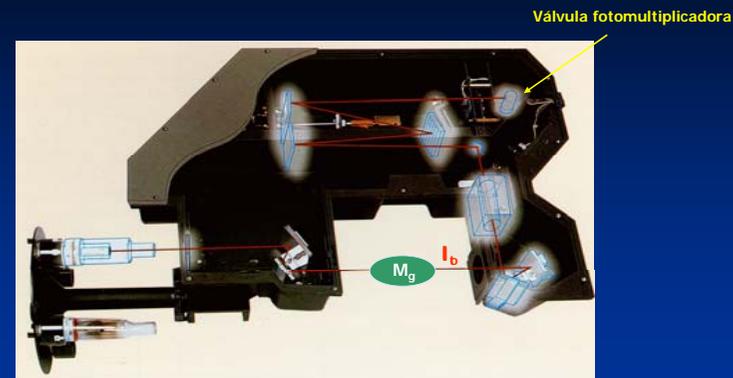
Espectrometria de absorção atômica



Montagem ótica de um espectrômetro de absorção atômica VARIAN



Montagem ótica de um espectrômetro de absorção atômica VARIAN



Aspectos históricos

► Sir Alan Walsh

(1945) fonte de radiação para absorção atômica

(1955) 1º trabalho de AA sobre a instrumentação

Walsh descobriu que a maioria dos átomos livres na chama se encontram no estado fundamental, muito pouco ionizados ou excitados.

A. Walsh, *Spectrochim. Acta*, 7 (1955) 108-117

► Cornelis Alkemade

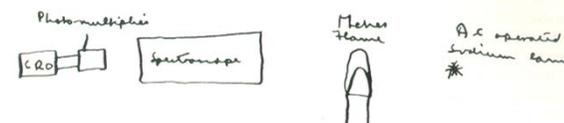
(1955) 1º trabalho sobre aplicação analítica de AA

C.T.J. Alkemade e J.M.W. Milatz, *J. Opt. Soc. Am.*, 45 (1955) 583-584

C.T.J. Alkemade e J.M.W. Milatz, *Appl. Sci. Res. Sect.*, 4 (1955) 289-299



Esboço do primeiro espectrômetro de absorção atômica idealizado por Alan Walsh (1955).

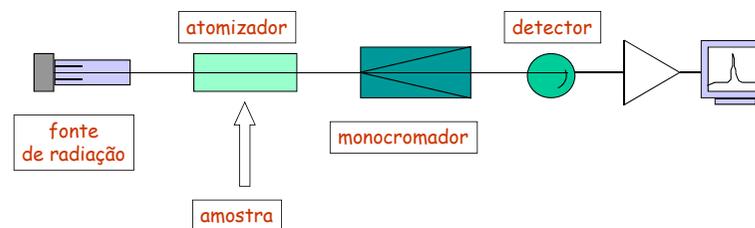


Varian AA-1 (1955)

► Primeiro instrumento de Absorção Atômica

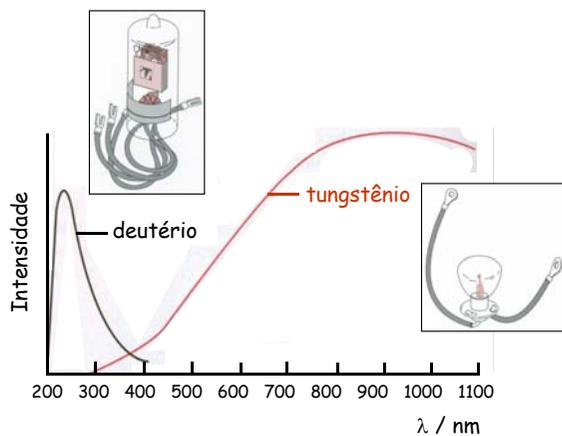


Espectrometria de absorção atômica



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Fontes de radiação (absorção molecular)



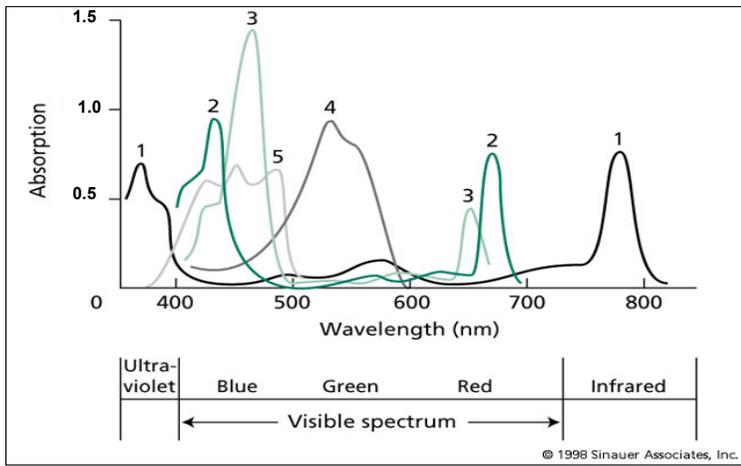
Espectros de emissão na região visível

Espectro contínuo (moléculas)

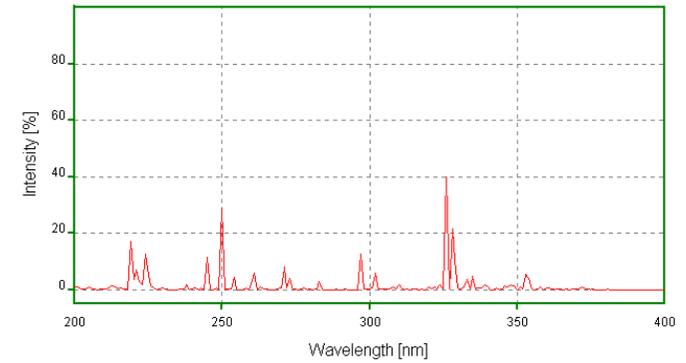


Espectro de linhas (átomos e/ou íons gasosos)





Espectro de emissão de cobre



- ✓ Kirchoff, 1860: relação entre emissão e absorção
- "Em condições especiais, todos os corpos podem absorver radiações que eles são capazes de emitir".

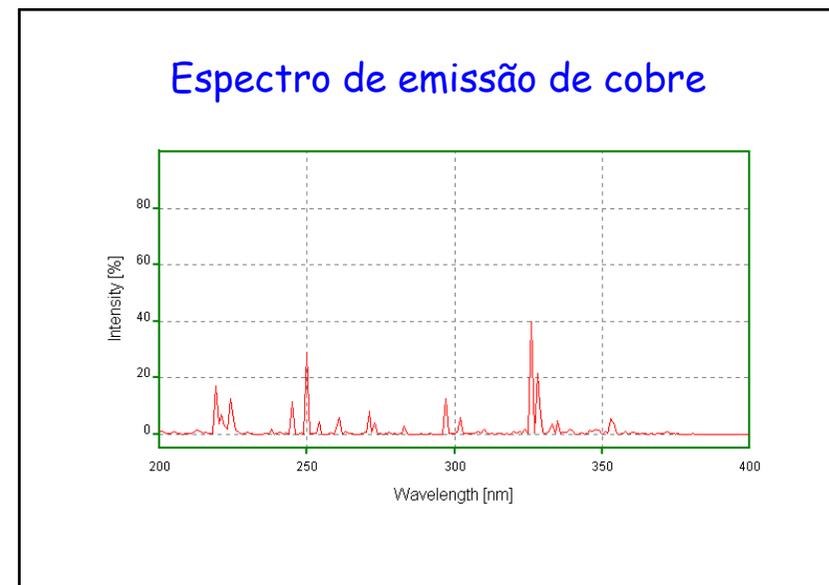
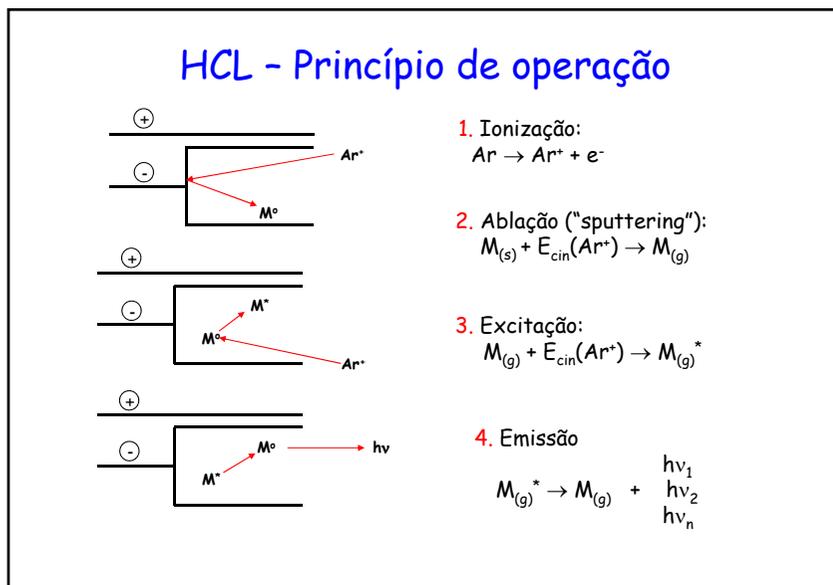
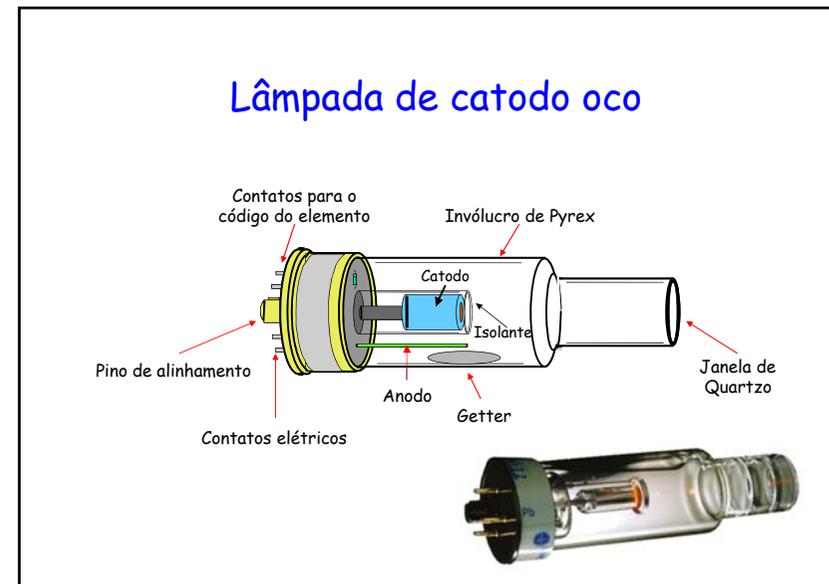
Fontes de radiação

- ✓ Lâmpada de catodo oco
(HCL - Hollow Cathode Lamp)
- ✓ Lâmpada de descarga sem eletrodos
(EDL - Electrodeless Discharge Lamp)

Table of Elements for Atomic Absorption

■ Hollow cathode lamps of these elements are available from PerkinElmer
 ■ Excimer discharge lamps of these elements are available from Fluorolite, Inc.
 ■ The hollow cathode discharge lamps of these elements are available from Denki-Chem.

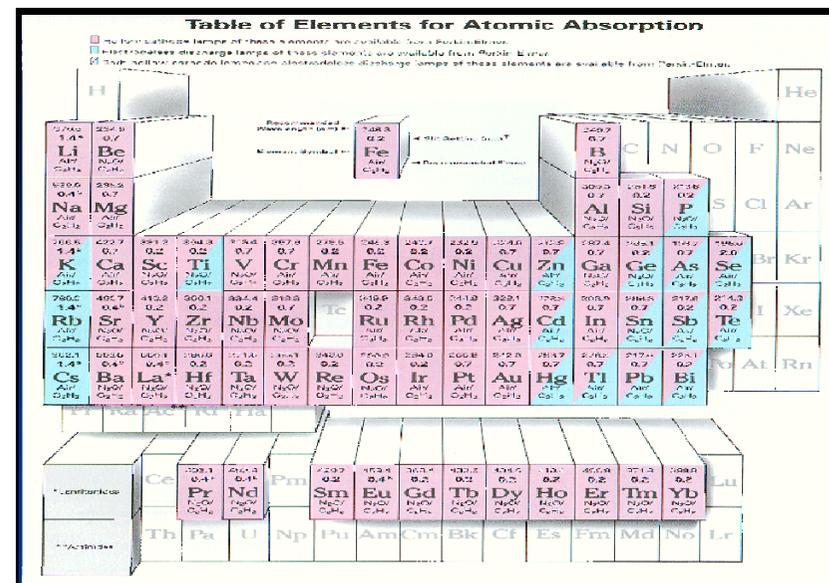
H	He																
Li 6.941 1.44 1.02 0.997	Be 9.012 1.57 1.02 0.997	B 10.811 2.44 1.02 0.997	C 12.011 2.00 1.02 0.997	N 14.007 3.04 1.02 0.997	O 15.999 3.54 1.02 0.997	F 18.998 4.04 1.02 0.997	Ne										
Na 22.990 0.97 0.997	Mg 24.305 1.30 0.97 0.997	Al 26.982 1.42 0.97 0.997	Si 28.086 1.48 0.97 0.997	P 30.974 1.50 0.97 0.997	S 32.06 1.54 0.97 0.997	Cl 35.453 1.59 0.97 0.997	Ar										
K 39.098 0.85 0.997	Ca 40.078 0.90 0.997	Sc 44.956 1.04 0.997	Ti 47.88 1.04 0.997	V 50.942 1.04 0.997	Cr 52.00 1.04 0.997	Mn 54.938 1.04 0.997	Fe 55.845 1.04 0.997	Co 58.933 1.04 0.997	Ni 58.69 1.04 0.997	Cu 63.546 1.04 0.997	Zn 65.38 1.04 0.997	Ga 69.723 1.04 0.997	Ge 72.64 1.04 0.997	As 74.922 1.04 0.997	Se 78.96 1.04 0.997	Br 79.904 1.04 0.997	Kr
Rb 85.468 0.82 0.997	Sr 87.62 0.85 0.997	Y 88.906 0.85 0.997	Zr 91.224 0.85 0.997	Nb 92.906 0.85 0.997	Mo 95.94 0.85 0.997	Tc	Ru 101.07 0.85 0.997	Rh 101.07 0.85 0.997	Pd 106.36 0.85 0.997	Ag 107.87 0.85 0.997	Cd 112.41 0.85 0.997	In 114.82 0.85 0.997	Sn 118.71 0.85 0.997	Sb 121.76 0.85 0.997	Te 127.60 0.85 0.997	I 126.905 0.85 0.997	Xe
Cs 132.905 0.79 0.997	Ba 137.33 0.82 0.997	La 138.905 0.82 0.997	Hf 178.49 0.82 0.997	Ta 180.948 0.82 0.997	W 183.84 0.82 0.997	Re	Os 190.23 0.82 0.997	Ir 192.22 0.82 0.997	Pt 195.08 0.82 0.997	Au 196.967 0.82 0.997	Hg 200.59 0.82 0.997	Tl 204.38 0.82 0.997	Pb 207.2 0.82 0.997	Bi 208.98 0.82 0.997	Po	At	Rn
Pr 140.908 0.82 0.997	Nd 144.24 0.82 0.997	Pm	Sm 150.36 0.82 0.997	Eu 151.96 0.82 0.997	Gd 157.25 0.82 0.997	Tb 158.925 0.82 0.997	Dy 162.50 0.82 0.997	Ho 164.930 0.82 0.997	Er 167.259 0.82 0.997	Tm 168.930 0.82 0.997	Yb 173.054 0.82 0.997	Lu					
Th 232.0377 0.82 0.997	Pa 231.03688 0.82 0.997	U 238.02891 0.82 0.997	Np 237.048173 0.82 0.997	Pu 244.064223 0.82 0.997	Am 243.061361 0.82 0.997	Cm 247.071373 0.82 0.997	Bk 247.071373 0.82 0.997	Cf 251.082888 0.82 0.997	Es 252.083316 0.82 0.997	Fm 257.103521 0.82 0.997	Md 258.103894 0.82 0.997	No 259.104267 0.82 0.997	Lr				



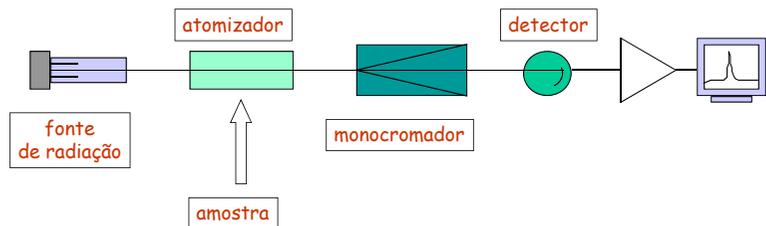
Exemplos de linhas utilizadas em AAS

Elemento	λ (nm)
Ni	232,0
	352,5*
	351,5
Cu	362,5
	342,8*
	327,4
	217,9
	218,2
Ca	222,6
	244,2
	422,7*
Cd	228,8*
Fe	248,3*

* Linhas de emissão de maior intensidade

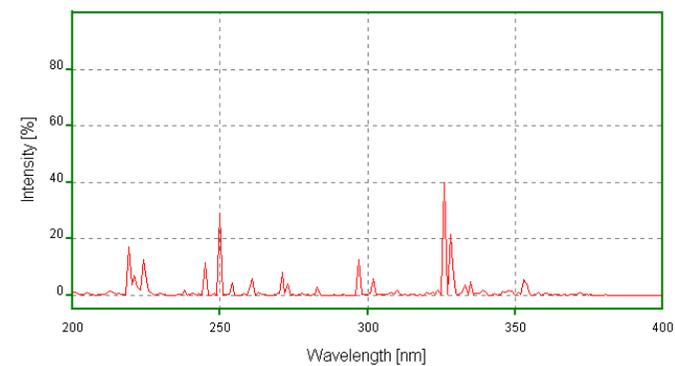


Espectrometria de absorção atômica

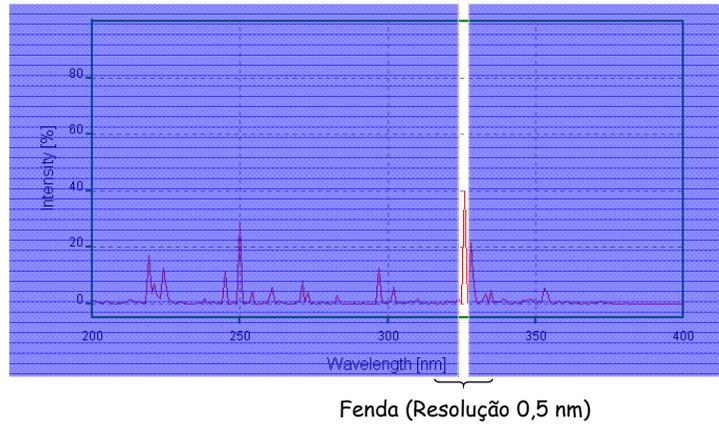


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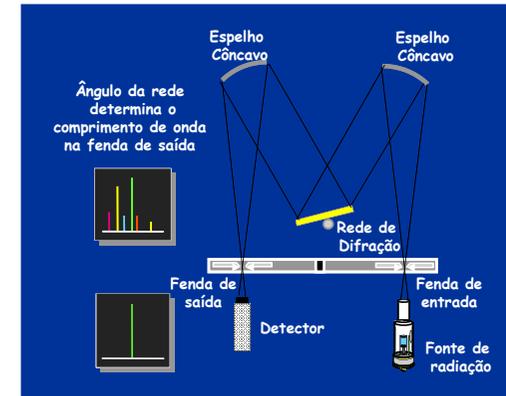
Espectro de emissão de cobre



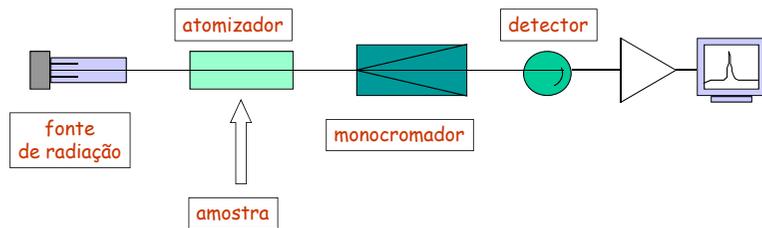
Espectro de emissão de cobre



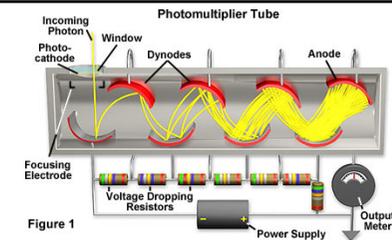
Monocromador Czerny-Turner



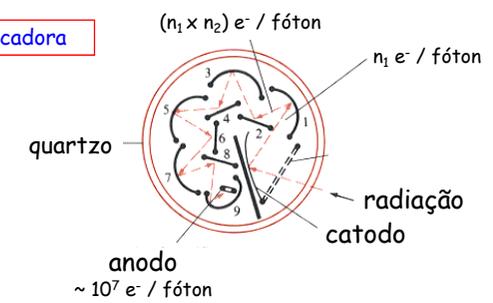
Espectrometria de absorção atômica



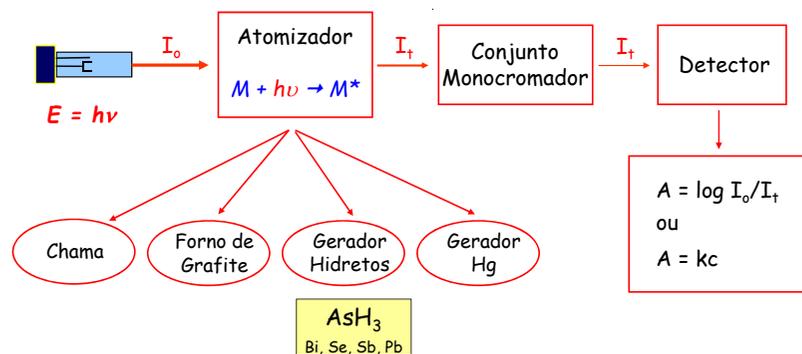
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fotomultiplicadora



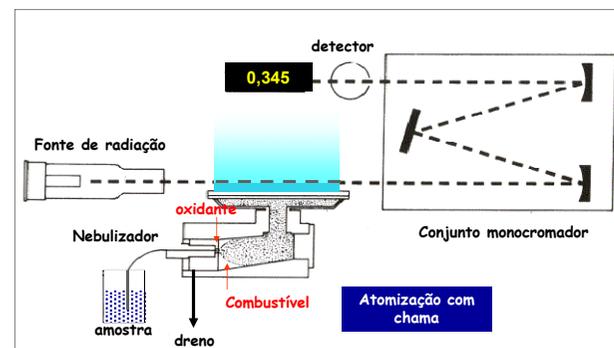
Espectrometria de absorção atômica



Atomizadores e temperaturas de atomização

- ▶ **Atomização com chama**
 C_2H_2 - ar (~ 2300 °C)
 C_2H_2 - N_2O (~ 3000 °C)
- ▶ **Atomização eletrotérmica**
 Forno de grafite (1400 a 3000 °C)
- ▶ **Geração de hidretos**
 Aquecimento do tubo com chama (1000 a 1400 °C)
 Aquecimento do tubo com forno (800 a 1000 °C)
- ▶ **Geração de vapor de mercúrio**
 A frio (redução a Hg^0 , temperatura ambiente)

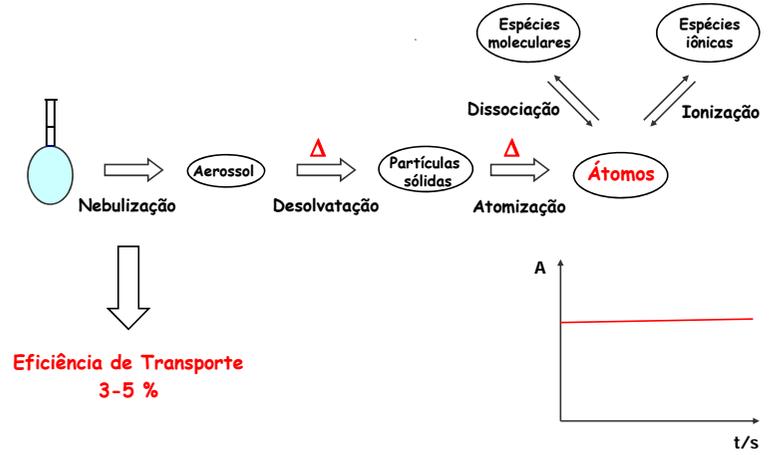
Atomização com chama





Queimador
Nebulizador

Absorção atômica com chama

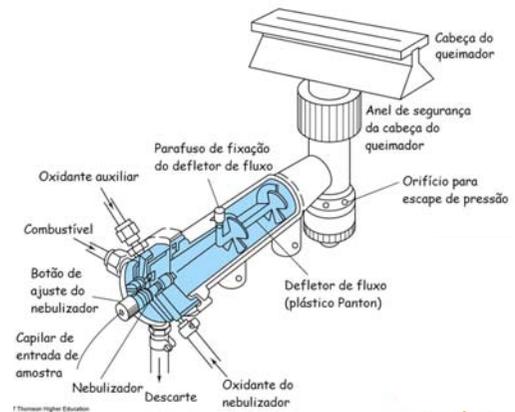


Nebulização

- ⇒ Produção de aerossol
- ⇒ Gotas com diâmetro < 5 μm
- ⇒ Eficiência < 5% (soluções aquosas)

“Calcanhar de Aquiles”

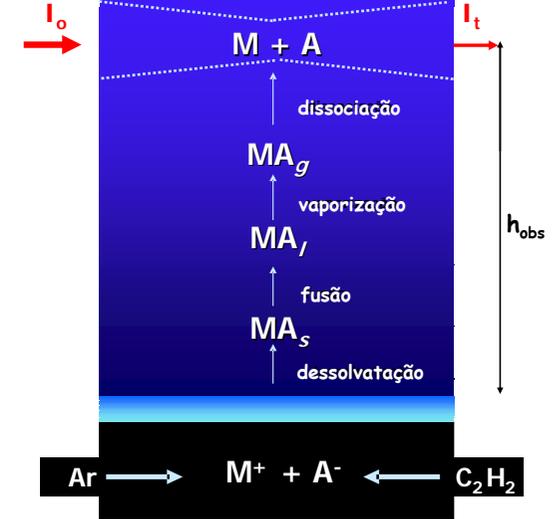
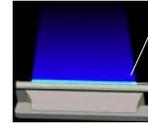
Conjunto nebulizador/queimador



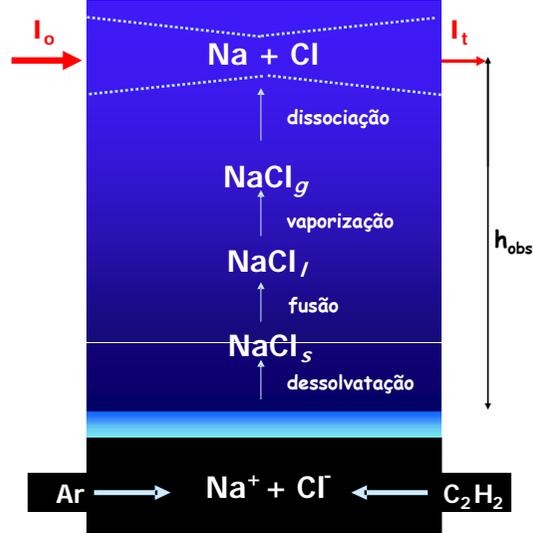
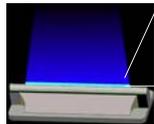


Queimador
Nebulizador

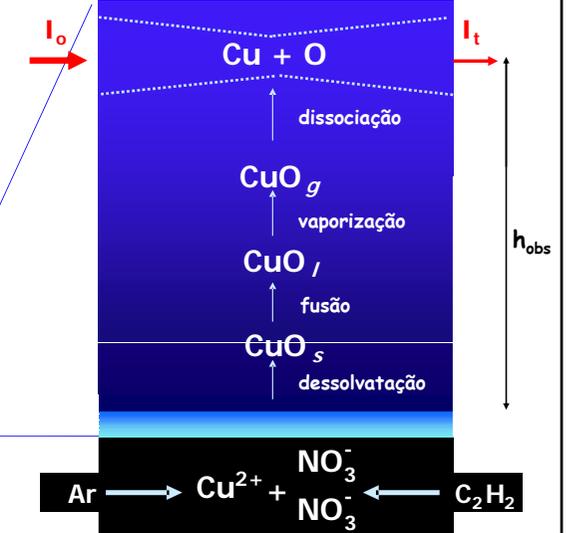
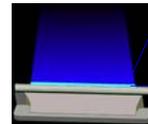
Atomização
na
chama



Atomização
na
chama:
via cloreto

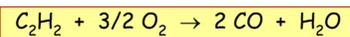


Atomização
na
chama:
via óxido



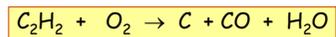
Composição de chama

✓ Chama estequiométrica (Ex.: 70 L/h C_2H_2 /450 L/h ar)



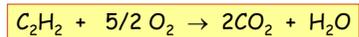
✓ Chama redutora (Ex.: 90 L/h C_2H_2 /450 L/h ar)

• Ex.: Be, Mg, Ca, Sr, Ba, Mo, Cr, Sn

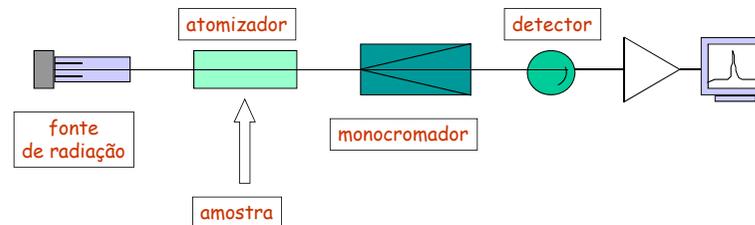


✓ Chama oxidante (Ex.: 50 L/h C_2H_2 /450 L/h ar)

• Ex.: Ag, Au, Zn

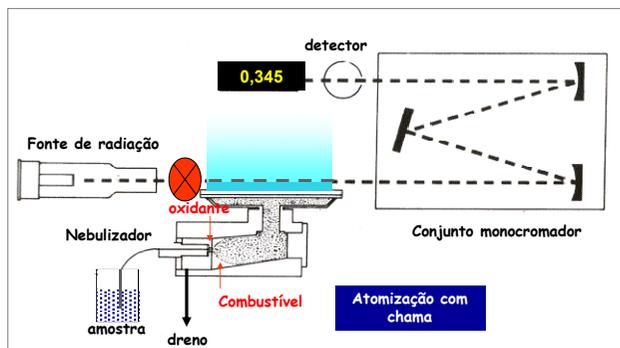


Espectrometria de absorção atômica



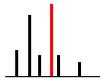
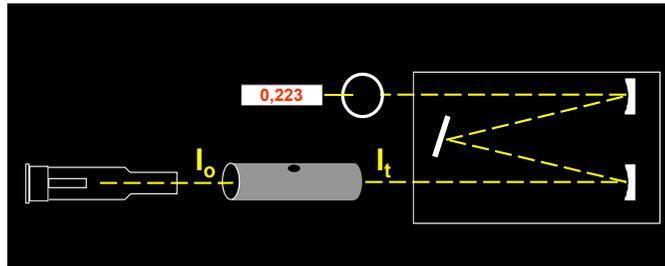
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Atomização em chama



Atomização eletrotérmica

GFAAS



— Linha de emissão da fonte de radiação para absorção atômica

— Linhas do gás de enchimento da fonte de radiação

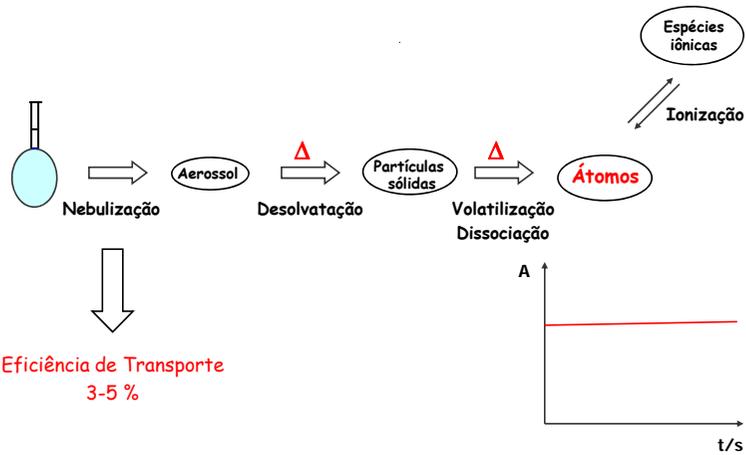
Cortesia VARIAN



✓ Boris L'vov

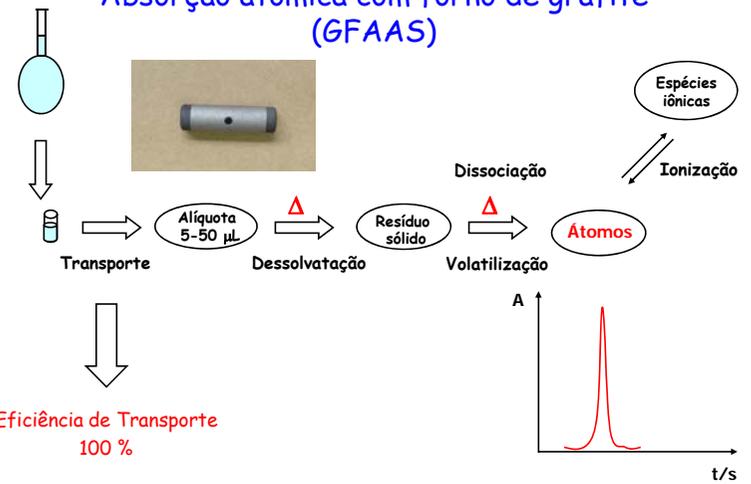
(1959) 1º trabalho de AA com atomização eletrotérmica

Absorção atômica com chama (FAAS)



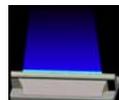
Eficiência de Transporte
3-5 %

Absorção atômica com forno de grafite (GFAAS)



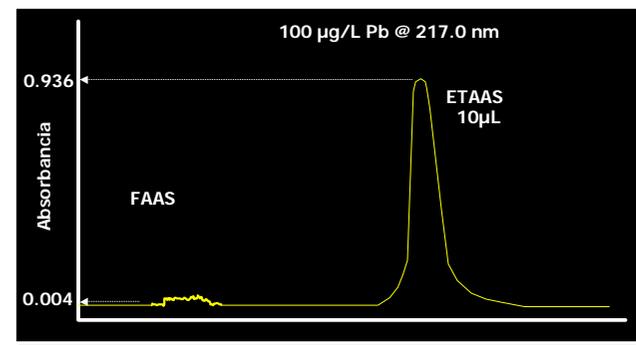
Eficiência de Transporte
100 %

chama x forno de grafite
átomos no volume de observação



atomização	íons em solução	átomos no volume de observação
na chama	100	1
no forno de grafite	100	100

Sinais absorção atômica de chumbo



Cortesia VARIAN

Limites de detecção em $\mu\text{g L}^{-1}$

Elemento	FAAS	ETAAS*	$LD_{\text{FAAS}}/LD_{\text{ETAAS}}$
Ag	3	0.04	75
As	450	0.25	1800
Bi	50	0.45	111
Cd	3	0.01	300
Cr	9	0.08	112
Pb	15	0.2	75
Zn	1.5	0.01	150

* volume injetado: 20 μL , corretor de fundo - D_2 , altura de pico

Cortesia VARIAN

Características da ETAAS

- ✓ excelente sensibilidade
- ✓ necessita de pequenas quantidades de amostra
- ✓ baixo consumo de soluções analíticas
- ✓ amostras líquidas, sólidas, gasosas e suspensões
- ✓ pré-tratamento térmico *in situ*

Forno de grafite Varian GTA-100



Tipos de Tubos de Grafite

Aquecimento longitudinal

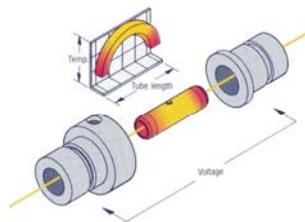


Aquecimento transversal

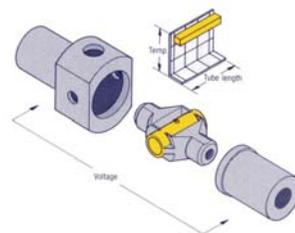


Atomizadores de grafite

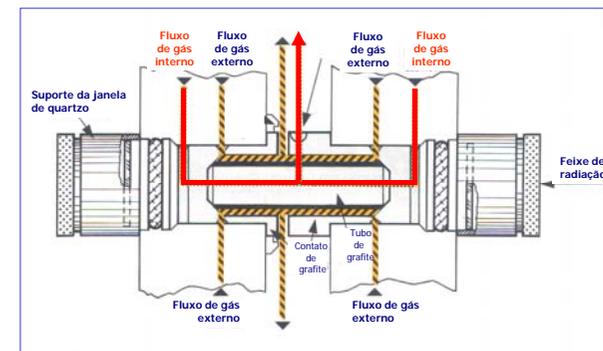
Aquecimento longitudinal



Aquecimento transversal

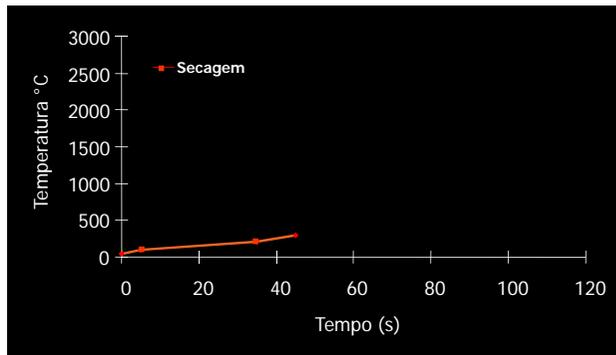


Forno de grafite com aquecimento longitudinal



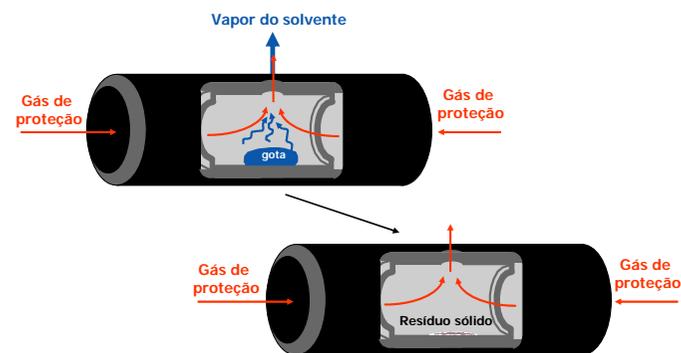
Adaptado de catálogo Perkin Elmer

Programa de aquecimento



Cortesia VARIAN

Etapa de secagem

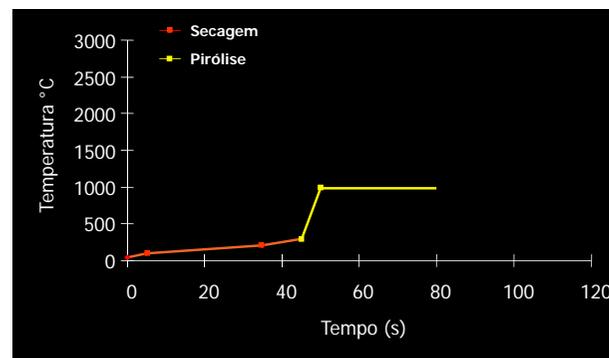


modificado a partir de slide da VARIAN

Secagem

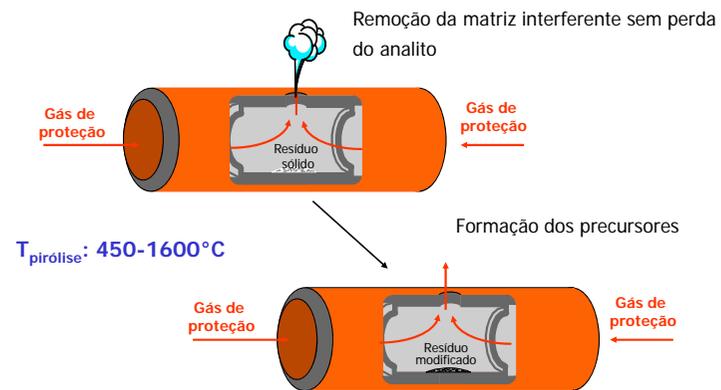


Programa de aquecimento



Cortesia VARIAN

Etapa de pirólise

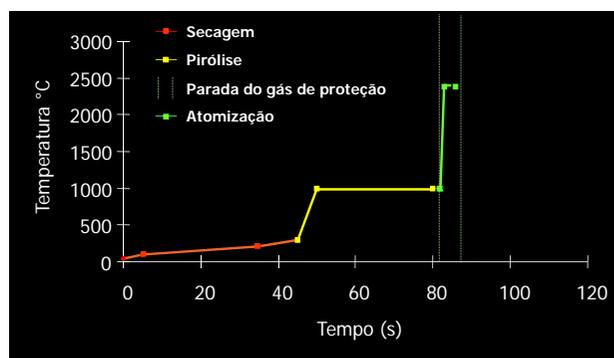


modificado a partir de slide da VARIAN

Pirólise

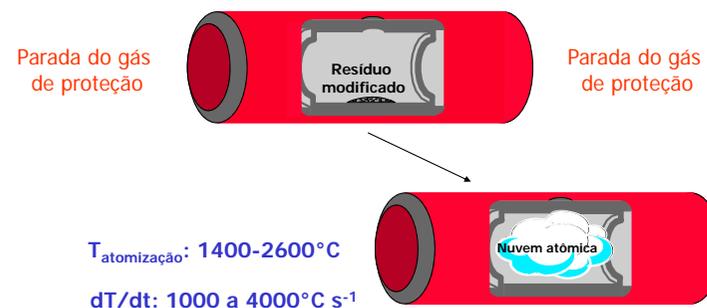


Programa de aquecimento



Cortesia VARIAN

Etapa de atomização

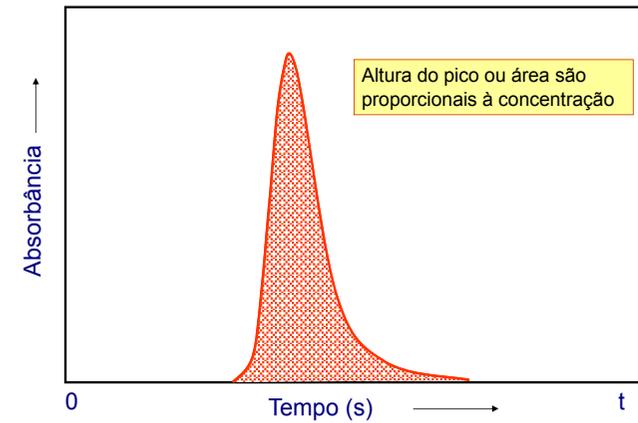


Adaptado de slide da VARIAN

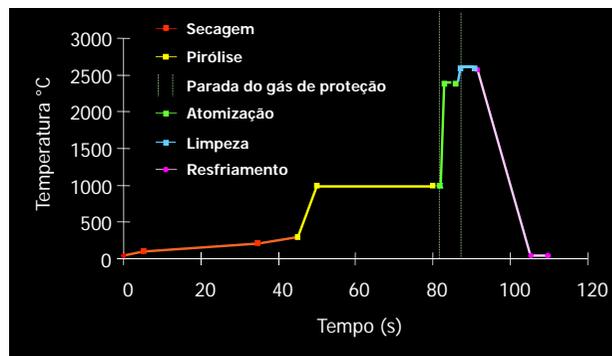
Atomização



Sinal analítico



Programa de aquecimento



Cortesia VARIAN

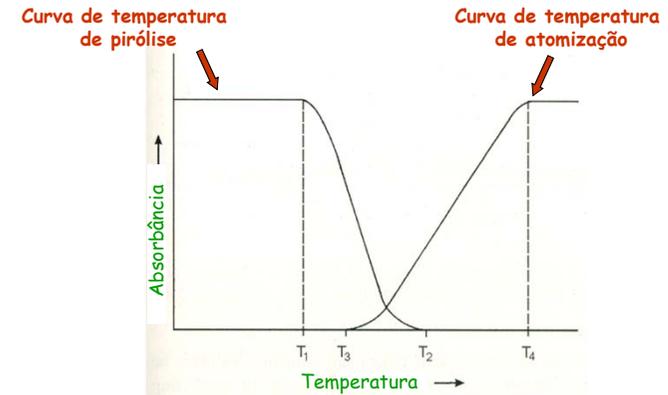
Programa de aquecimento

- ✓ **Secagem** - remoção do solvente, ácido ou azeótropo
- ✓ **Pirólise** - separação do analito de componentes da matriz
- ✓ **Atomização** - vaporização do analito e medida
- ✓ **Limpeza** - remoção de espécies remanescentes
- ✓ **Resfriamento** - adequar o forno para introdução da próxima amostra

Programa de Aquecimento

Etapa	T (°C)	Rampa (°C s ⁻¹)	Patamar (s)	Vazão Ar (mL/min)	Leitura
Secagem I	100	10	20	250	Não
Secagem II	130	5	10	250	Não
Pirólise	T _p	100	10	250	Não
Atomização	T _a	Max	5	0	Sim
Limpeza	2500	1200	2	250	Não

Otimização do programa de aquecimento



Desgaste do tubo



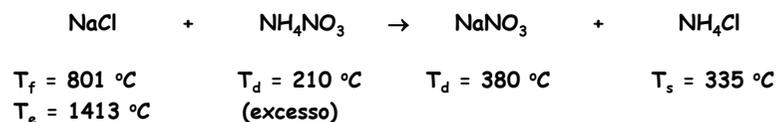
Modificador químico

Substância introduzida no tubo de grafite, simultaneamente ou não com a solução analítica, visando minimizar efeitos de matriz.

- ✓ Estabilizar termicamente o analito
- ✓ Desestabilizar os componentes da matriz

Modificador químico

► Determinação de Cu em água de mar



R.D. Ediger, G.E. Peterson, J.D. Kerber, *At. Absorpt. Newsletter*, 13/3 (1974) 61

Modificador químico em solução

⇒ modificador químico "universal": $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$



⇒ modificador químico para Cd e Pb: $\text{NH}_4\text{H}_2\text{PO}_4 + \text{Mg}(\text{NO}_3)_2$

Welz, B., Schelemmer, G., Mudakavi, J.R., *J. Anal. At. Spectrom.*, 1992, 7, 1257-1270.

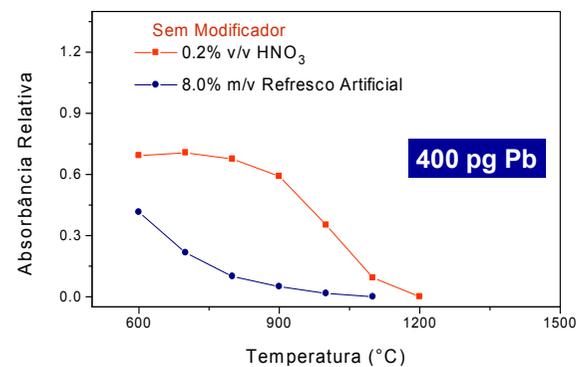
Direct determination of lead in sweet fruit-flavored powder drinks by electrothermal atomic absorption spectrometry

Lima EC, Krug FJ, Arruda MAZ
SPECTROCHIMICA ACTA PART B 53: (4) 601-611, 1998

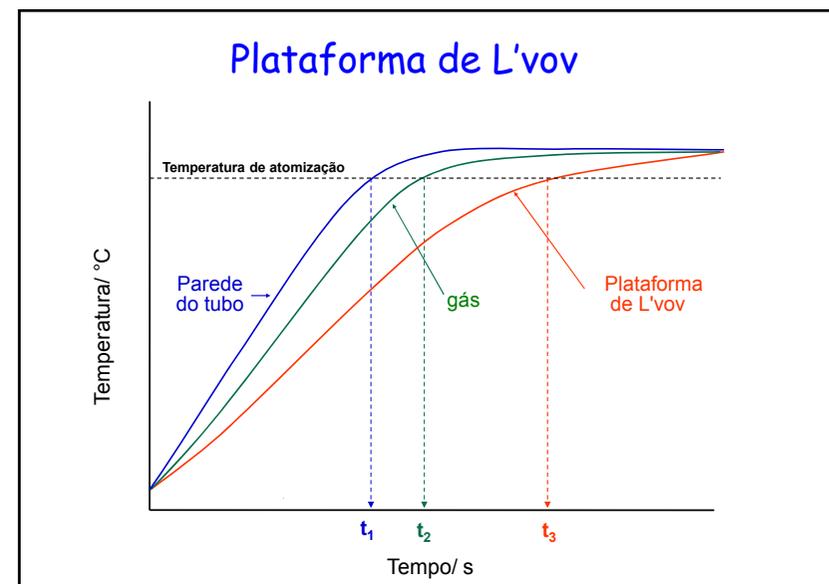
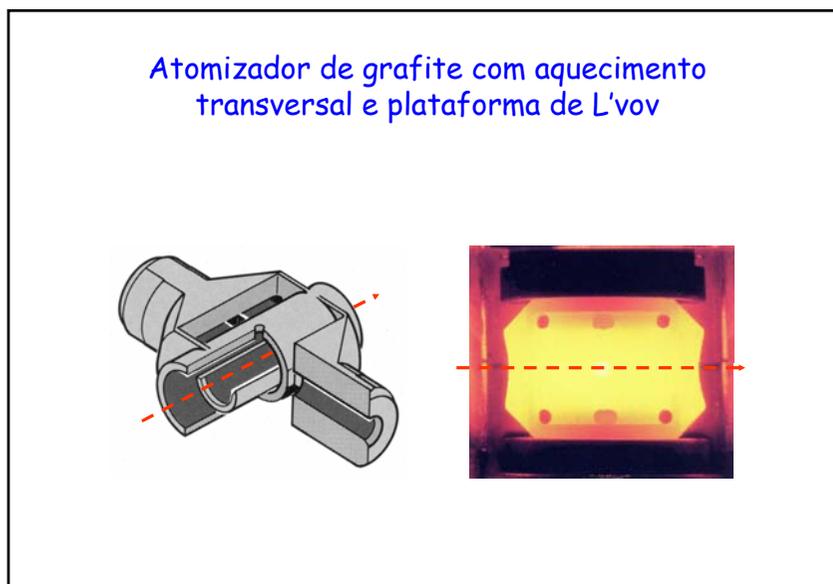
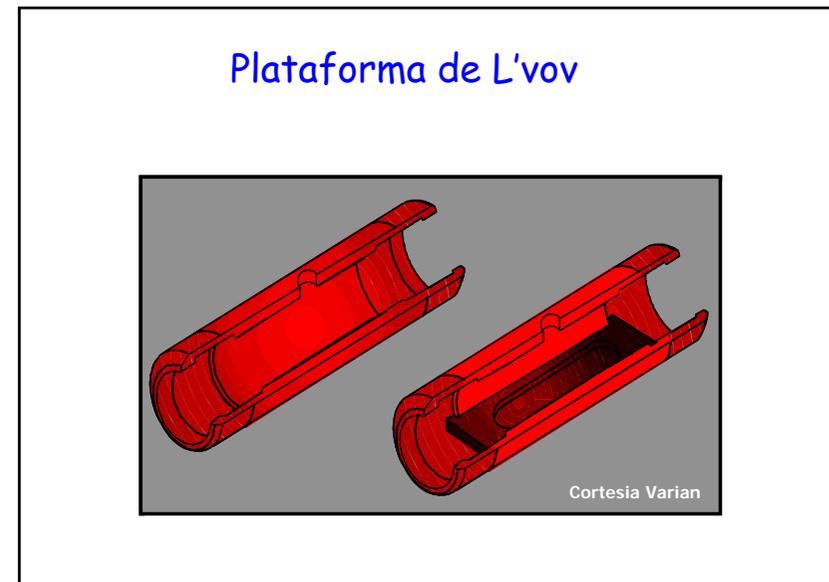
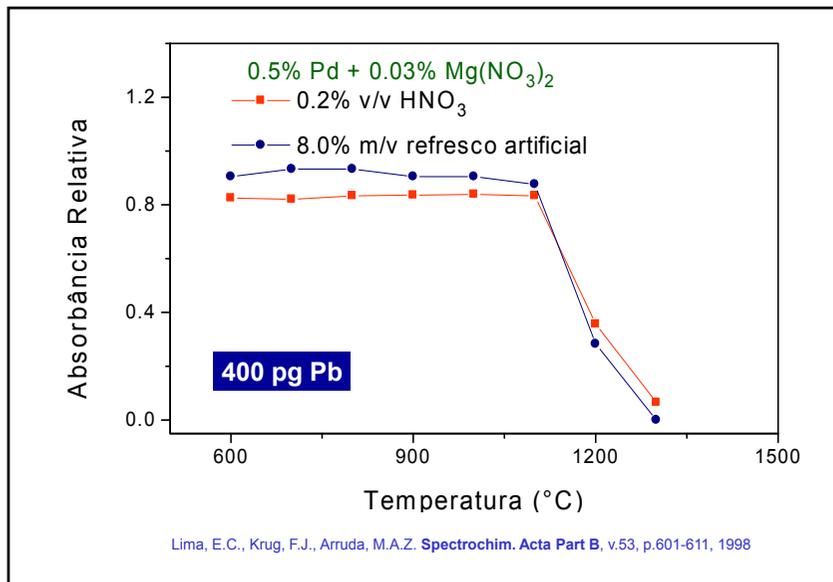
Abstract:

A simplified method for direct determination of lead in sweet fruit-flavored powder drinks, syrups and honeys by electrothermal atomic absorption spectrometry without sample digestion is proposed. Samples were dissolved in water, acidified to 0.2% (v/v) HNO₃, and directly injected into an end-capped transversely heated graphite atomizer (THGA). Building up of carbonaceous residue inside the atomizer was effectively precluded for sugar solutions not exceeding 8.0% (m/v) when a heating program with two pyrolysis steps (600 and 1000 °C) was carried out without air-ashing. Under these conditions one atomizer supported about 250 firings. Among various chemical modifiers tested, better recovery and repeatability results were obtained with a 5 μg Pd + 3 μg Mg(NO₃)₂ mixture. Tests carried out with individual concomitants containing up to 1.0 μg Na, K, Ca or Cl, and up to 10.0 μg phosphate or sulphate, and several mixtures of these six concomitants, did not reveal significant interferences on lead atomization. Characteristic mass and detection limit based on integrated absorbance were 15 and 11 μg Pb, respectively. The relative standard deviation based on 10 measurements for typical samples (20-60 μg g⁻¹ Pb) was always lower than 5.5%. The detection limit of 7.0 ng g⁻¹ Pb attained the Coder recommendation for the maximum allowed lead contents in the sugar samples. Application of t-test to the results obtained by the proposed direct analysis, and the official method adopted by Food Chemical Coder, demonstrated that there were no significant differences at the 5% probability level.

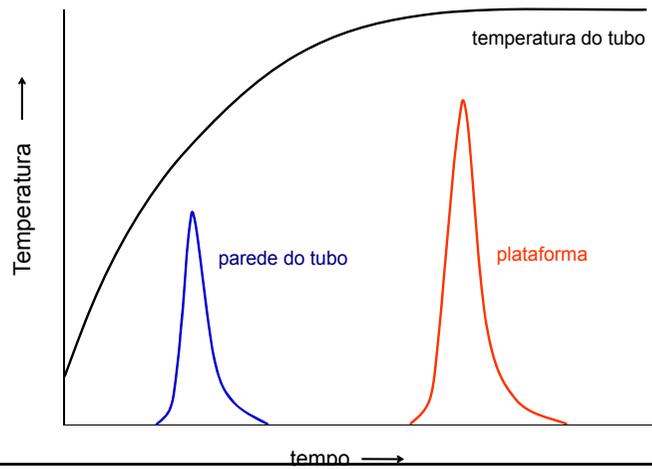
Determinação de chumbo em amostras com alto teor de açúcar



Lima, E.C., Krug, F.J., Arruda, M.A.Z. *Spectrochim. Acta Part B*, v.53, p.601-611, 1998



Plataforma de L'vov



Stabilized Temperature Platform Furnace (Condições STPF)

- ✓ plataforma de L'vov
- ✓ parada do gás na etapa de atomização
- ✓ medidas em absorbância integrada
- ✓ alta taxa de aquecimento
- ✓ eletrônica compatível com o sinal transiente
- ✓ modificadores químicos
- ✓ correção de fundo