



UNIVERSIDADE
DE SÃO PAULO
Instituto de Física de São Carlos



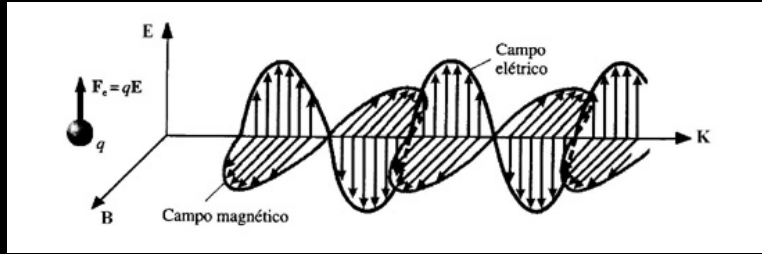
LLA IFSC-USP
LABORATÓRIO DE
LASER E APLICAÇÕES

Espectroscopia Óptica

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Espectro Eletromagnético



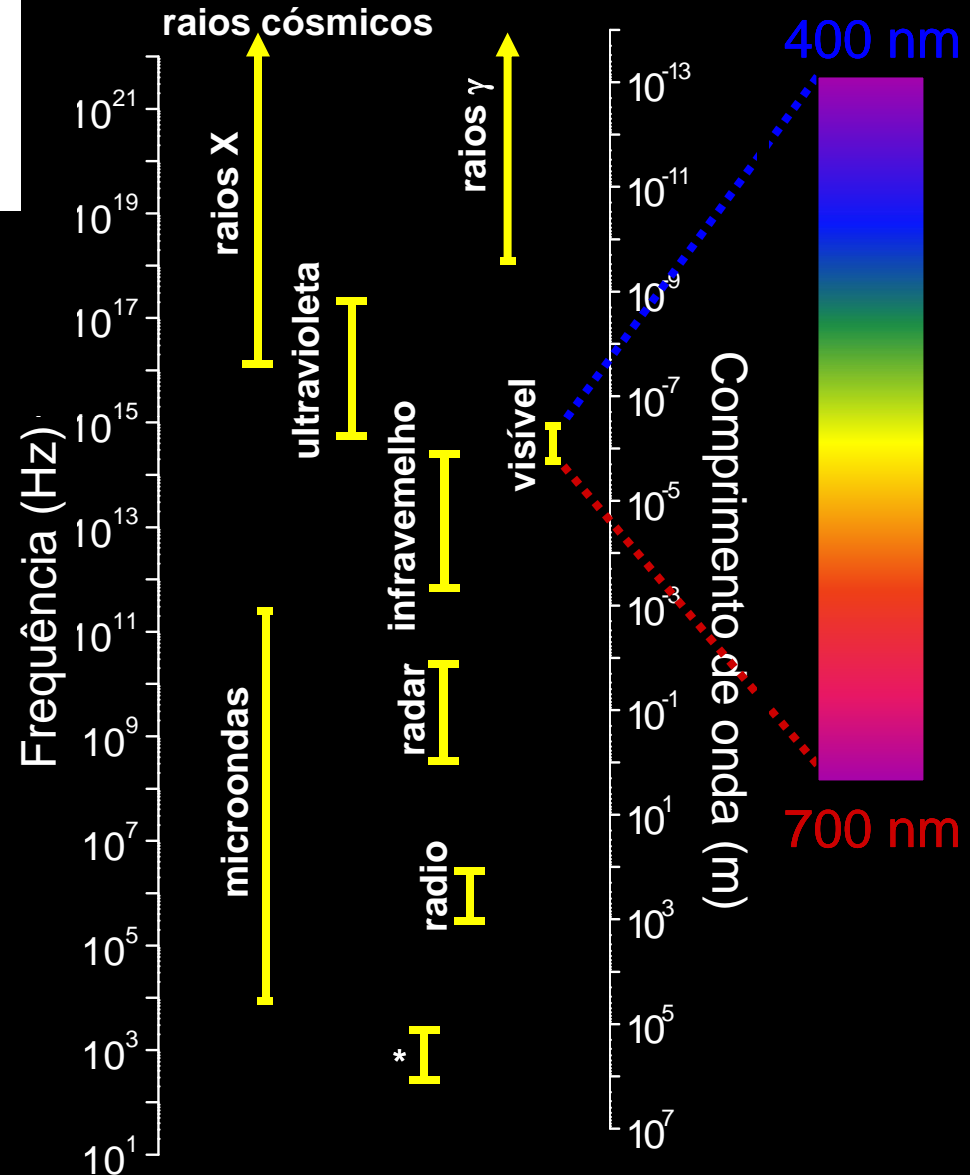
Equações de Maxwell

$$\nabla \cdot E = \rho / \epsilon_0$$

$$\nabla \cdot B = 0$$

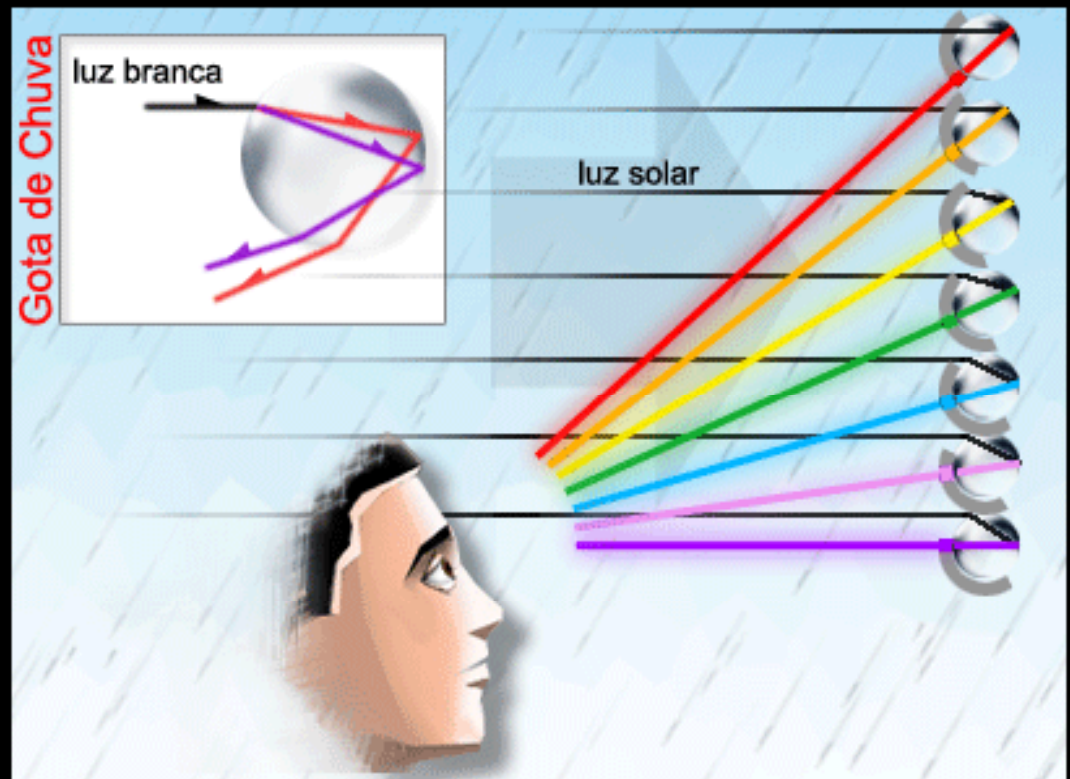
$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \mu_0 \epsilon_0 \frac{\partial E}{\partial t} + \mu_0 J$$



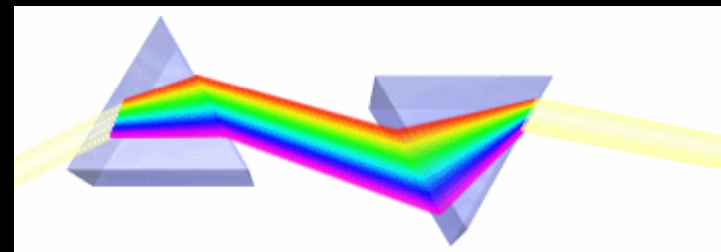
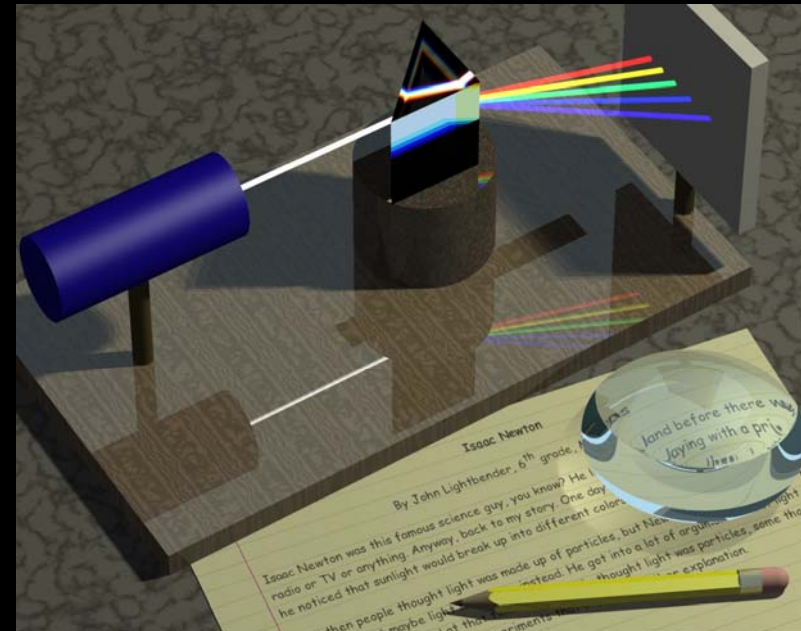
Historia da Espectroscopia

Decomposição da Luz



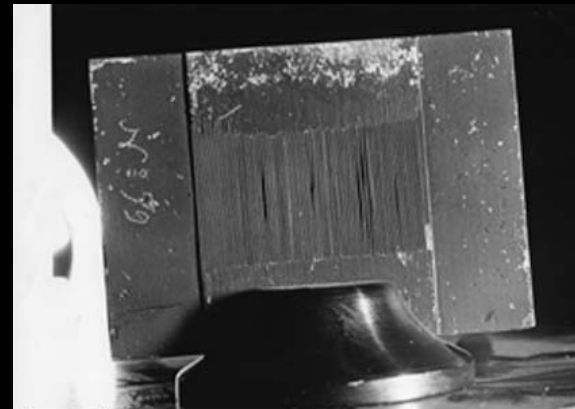
1665-1666

Isaac Newton (Físico Inglês)

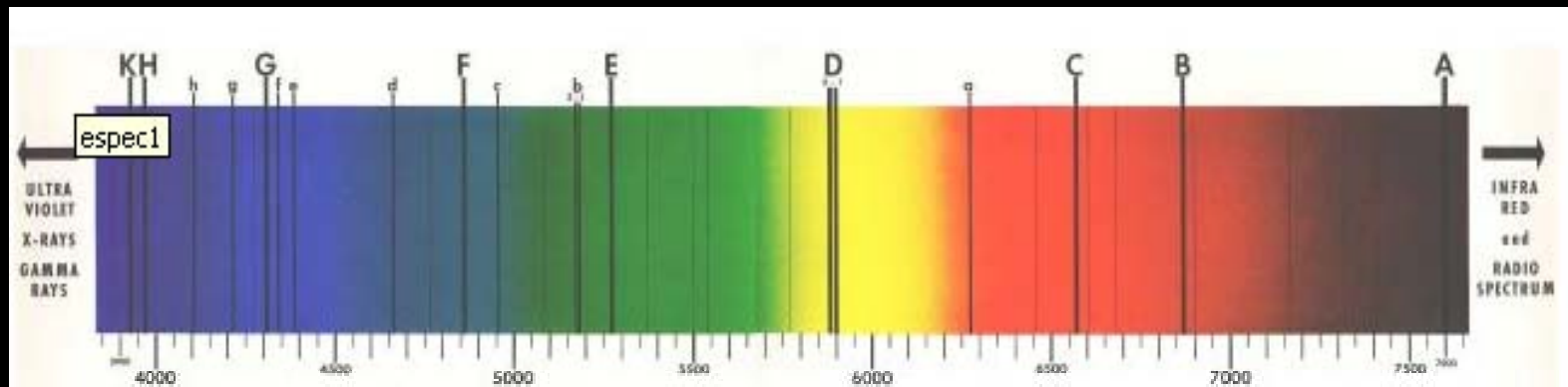




1814 Joseph von Fraunhofer repetiu a experiência de Newton



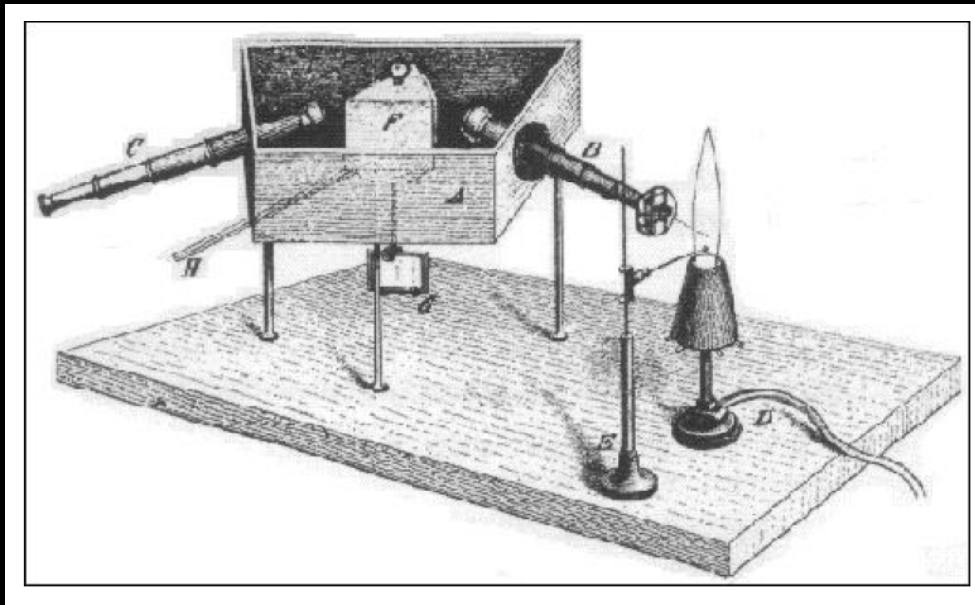
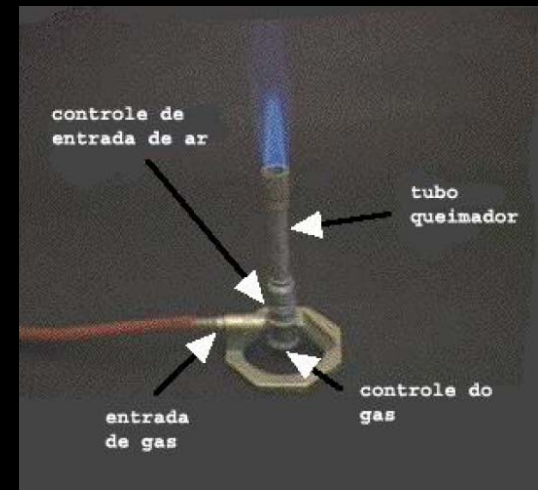
Scanned at the American Institute of Physics



Fraunhofer Identificou mais de 600 linhas Inclusive as linhas D do Sódio

Por volta de 1857 o químico alemão **Robert Wilhem Bunsen** inventou um queimador a gás, conhecido como “bico de Bunsen”

Em 1859 Bunsen e **Gustav Kirchhoff** construíram o primeiro espectroscópio com a finalidade de entenderem as observações de **Fraunhofer**



Cada elemento químico mostra um espectro com um arranjo único de linhas brilhantes

Hot blackbody



Prism



Continuous spectrum

a

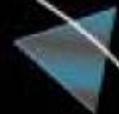
Cloud of cooler gas

Prism

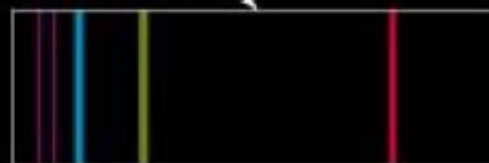


Absorption line spectrum

b



Prism



Emission line spectrum

c

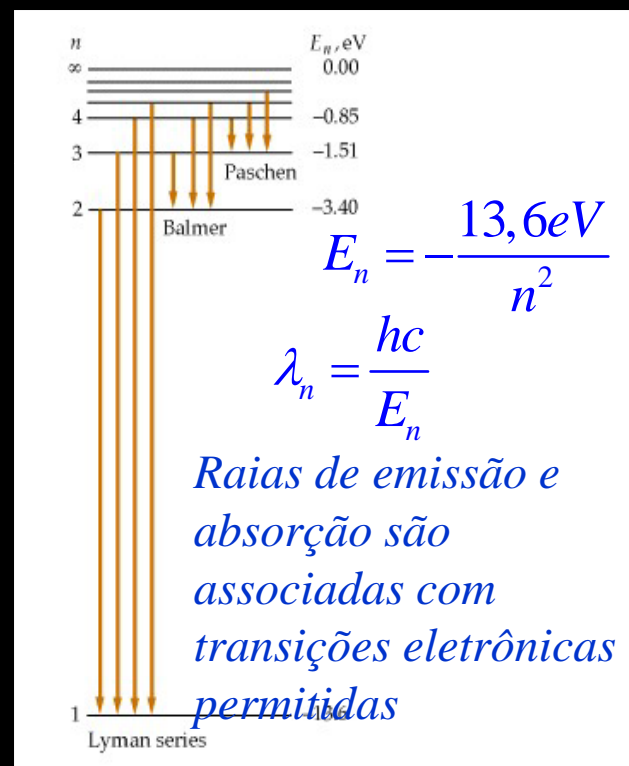
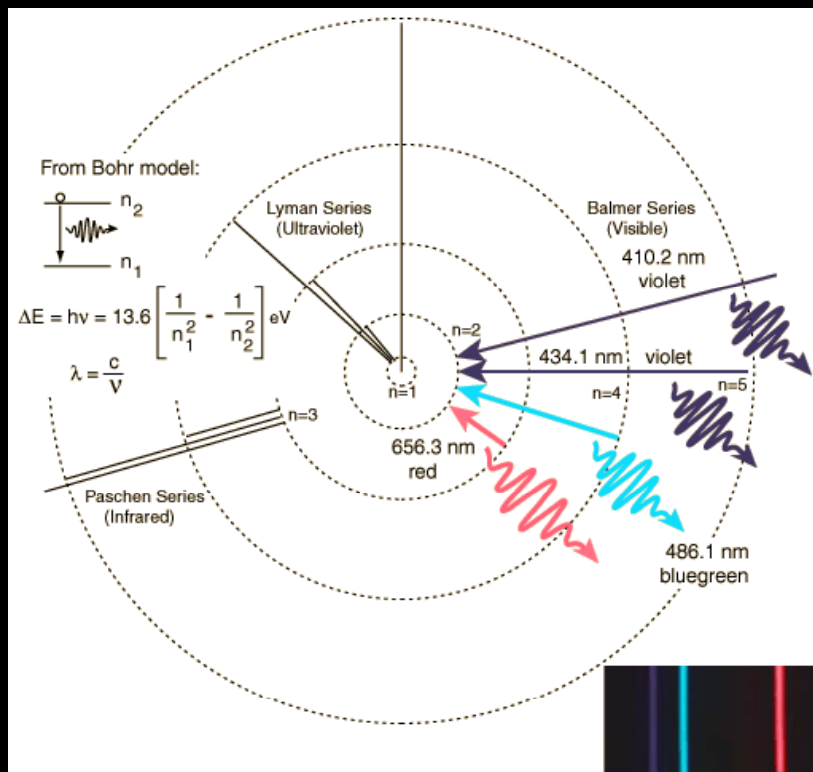
Em 1860 Bunsen e Kirchhoff identificaram uma nova linha no azul em amostra de água mineral, assim descobriram o **Césio**. Que do latim “caesium”, que significa azul-acinzentado.

No ano seguinte descobriram um conjunto de linhas na região do vermelho, assim esta descoberto o **Rubídio**. Que do latim “rubidium”, significa vermelho.

Durante a eclipse solar de 1868 alguns astrônomos decidiram fazer uma análise espectral da luz proveniente da parte mais externa do sol, assim descobriram o **Helio**, palavra derivada do grego “helios” que significa sol

Somente em 1895 o Hélio foi observado na Terra pelo escocês William Ramsay.

Em 1913 o físico dinamarquês **Niels Bohr** propôs um modelo para o átomo de hidrogênio que combinava os trabalhos de **Max Planck**, **Albert Einstein**, e **Ernst Rutherford**.



Apesar das emissões discretas serem utilizadas na caracterização qualitativa e quantitativa de elementos e substâncias, a origem física dessas emissões não eram entendidas.

Modelo de Bohr

Átomo de Hidrogênio

Formulado sobre Postulados Específicos

1925-1926

Werner Karl Heisenberg

Erwin Ruldolf Josef Alexander Schrodinger

MECÂNICA QUÂNTICA

Sistemas Atômicos



Exemplos de Espectros Atômicos:



Hidrogênio



Nitrogênio



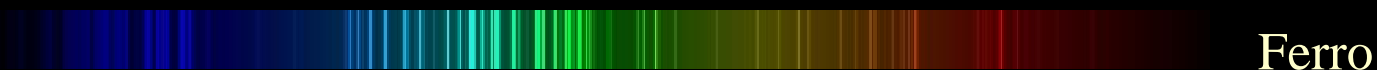
Oxigênio



Carbono



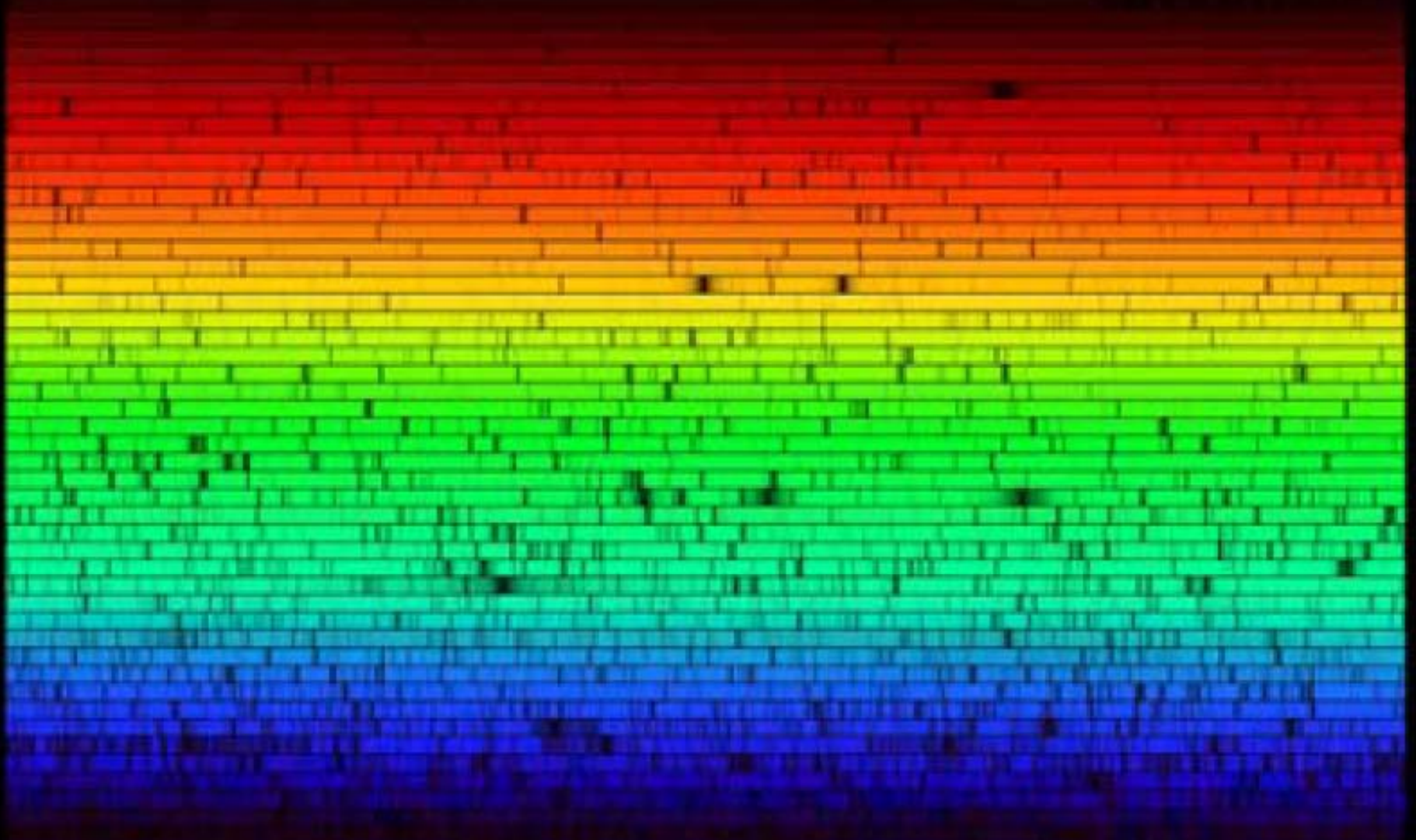
Argônio



Ferro

Espectro Solar

Observado com um Espectrômetro de Alta Resolução



Como Fazer Espectroscopia

Analisar a Composição da Radiação

Domínio da Freqüência

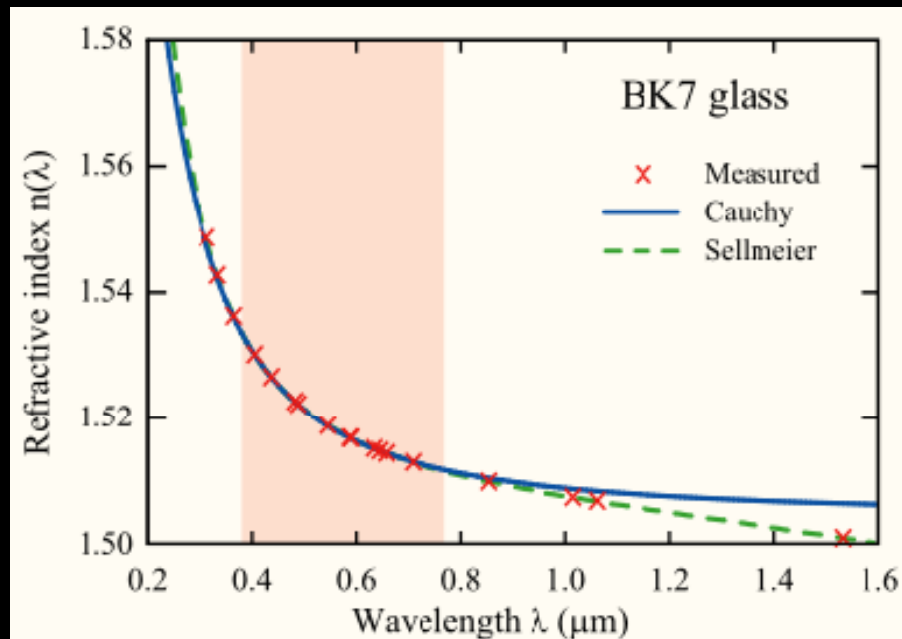
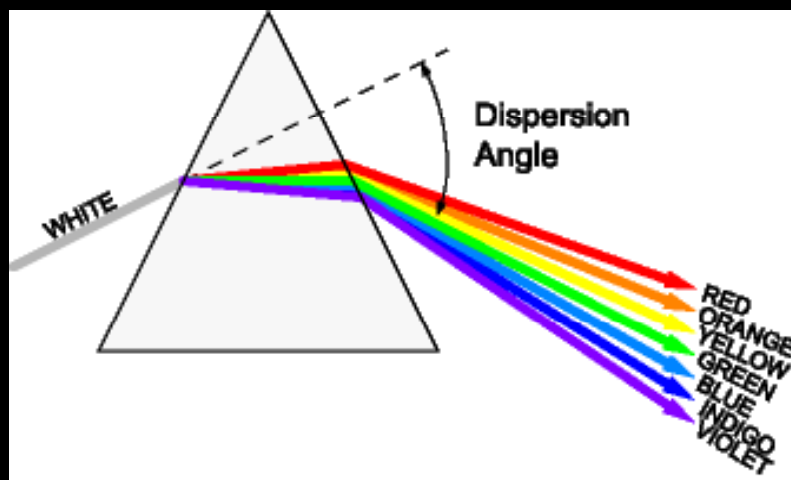
Domínio do Tempo

Refração

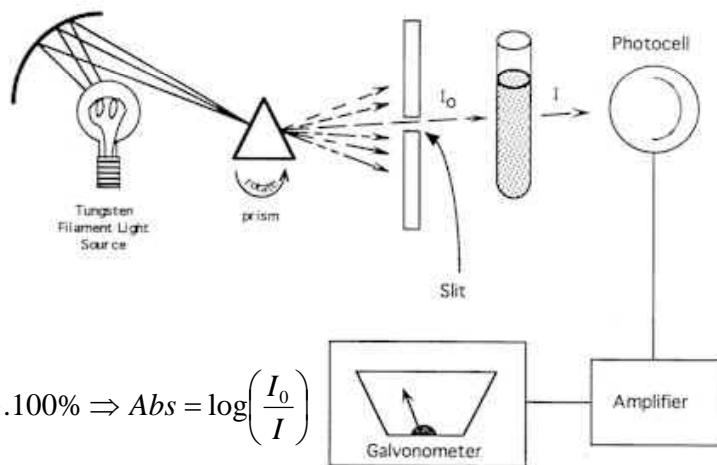
$$n_1 \text{sen}(\theta_1) = n_2 \text{sen}(\theta_2)$$

Refracção

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$



DESIGN OF A SPECTROPHOTOMETER



$$I = I_0 e^{-\alpha x} \Rightarrow T = \frac{I}{I_0} \cdot 100\% \Rightarrow Abs = \log\left(\frac{I_0}{I}\right)$$



Como Fazer Espectroscopia

Analisar a Composição da Radiação

Domínio da Freqüência

Domínio do Tempo

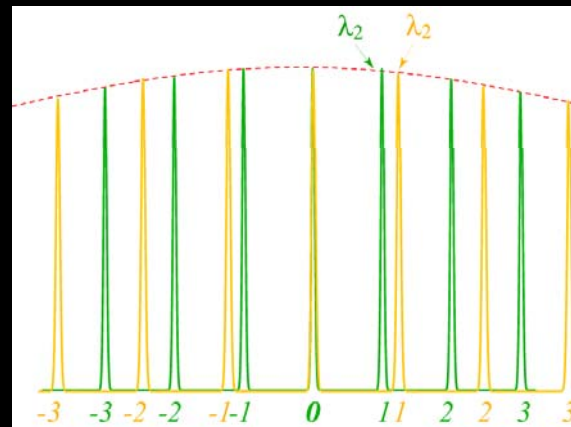
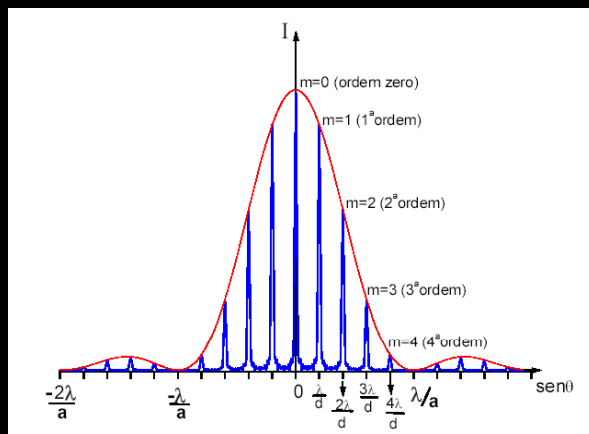
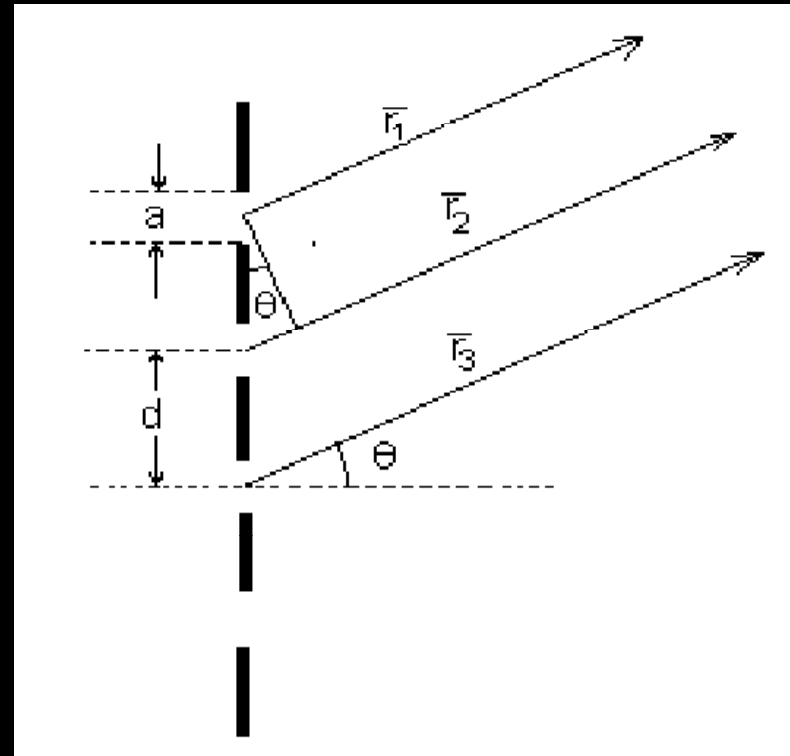
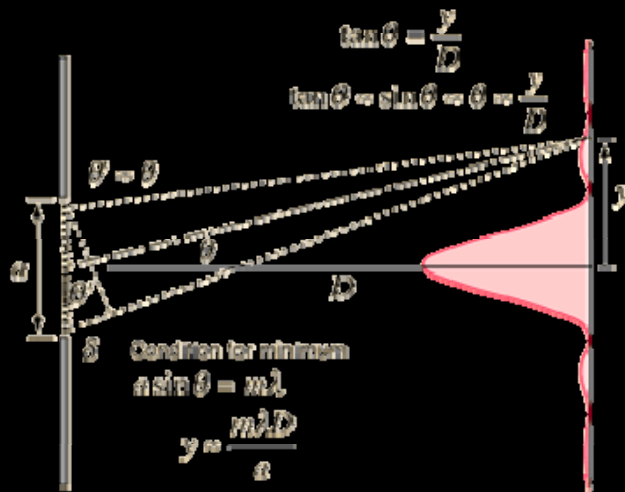
Refração

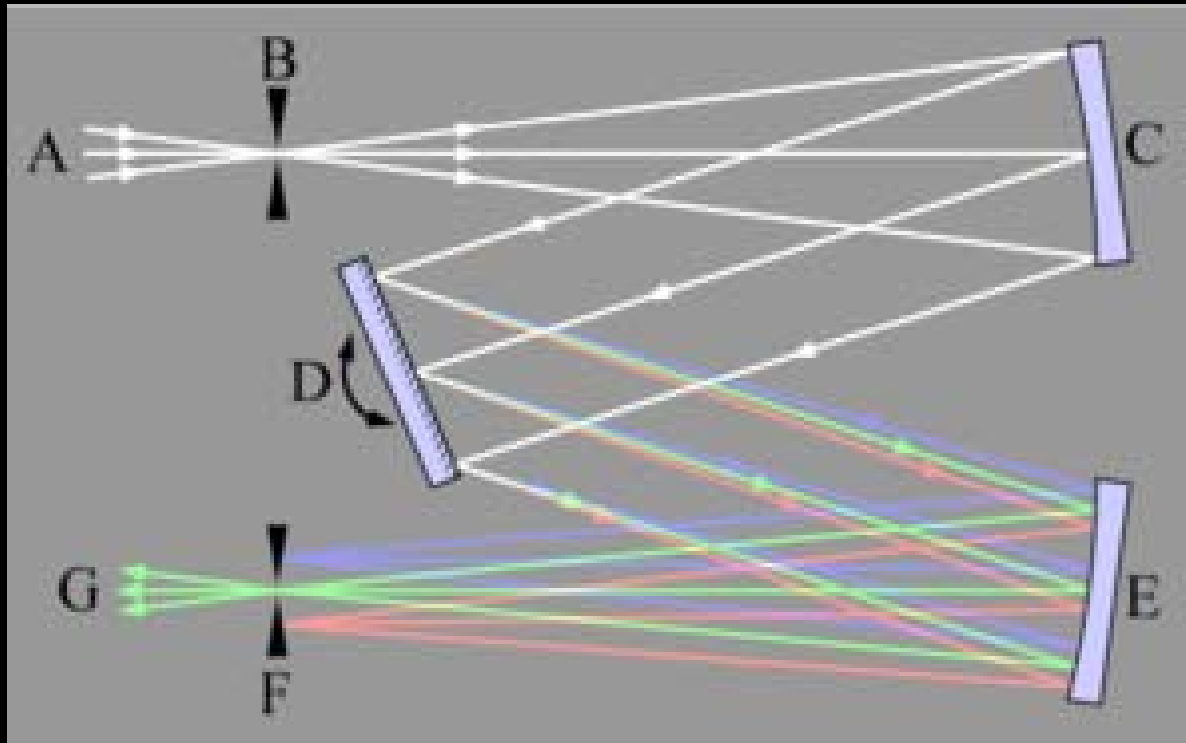
Difração

$$n_1 \text{sen}(\theta_1) = n_2 \text{sen}(\theta_2)$$

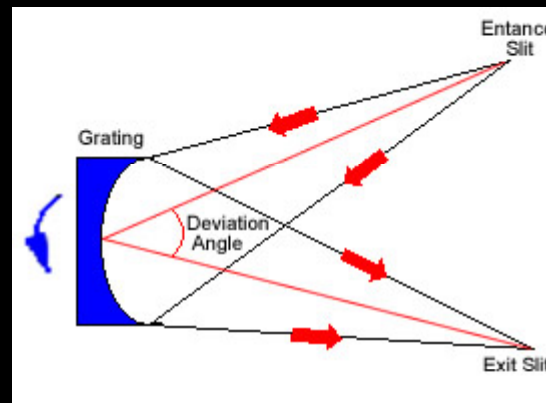
$$m\lambda = d \text{sen}(\theta)$$

Difração

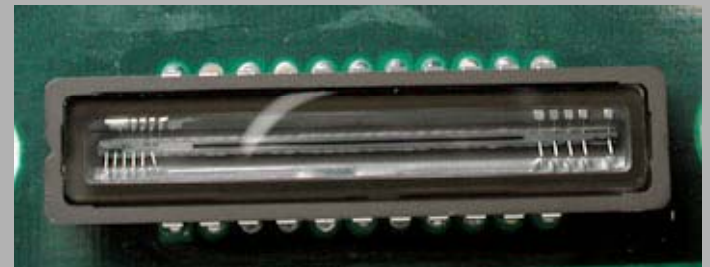
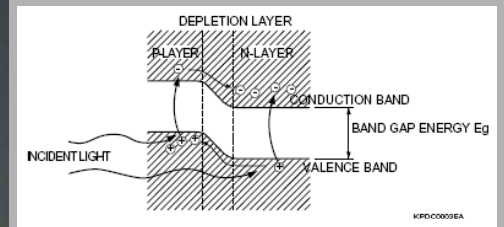
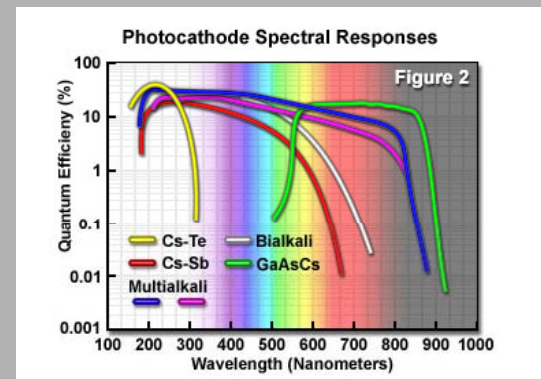
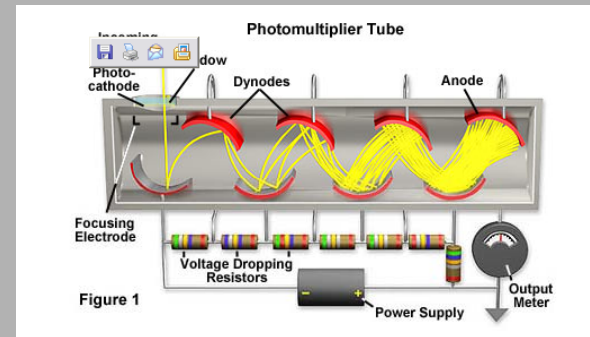
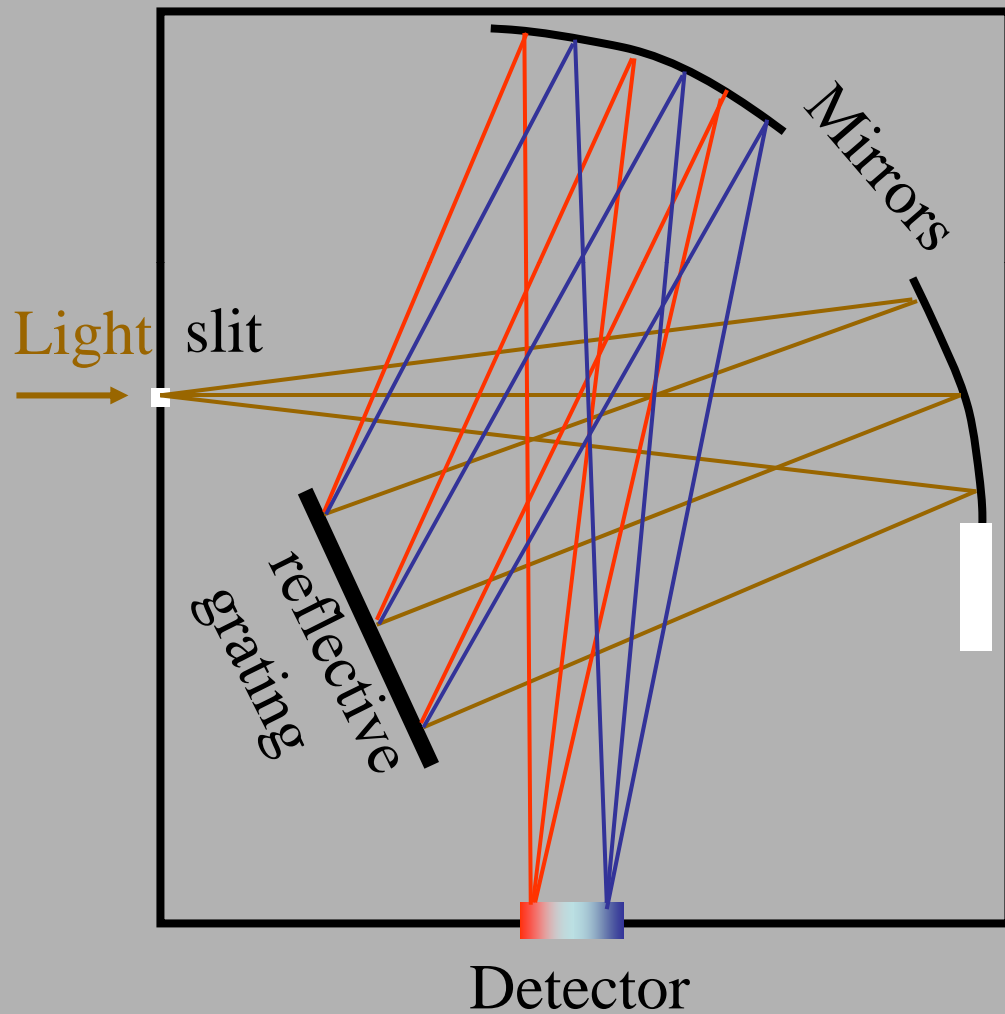


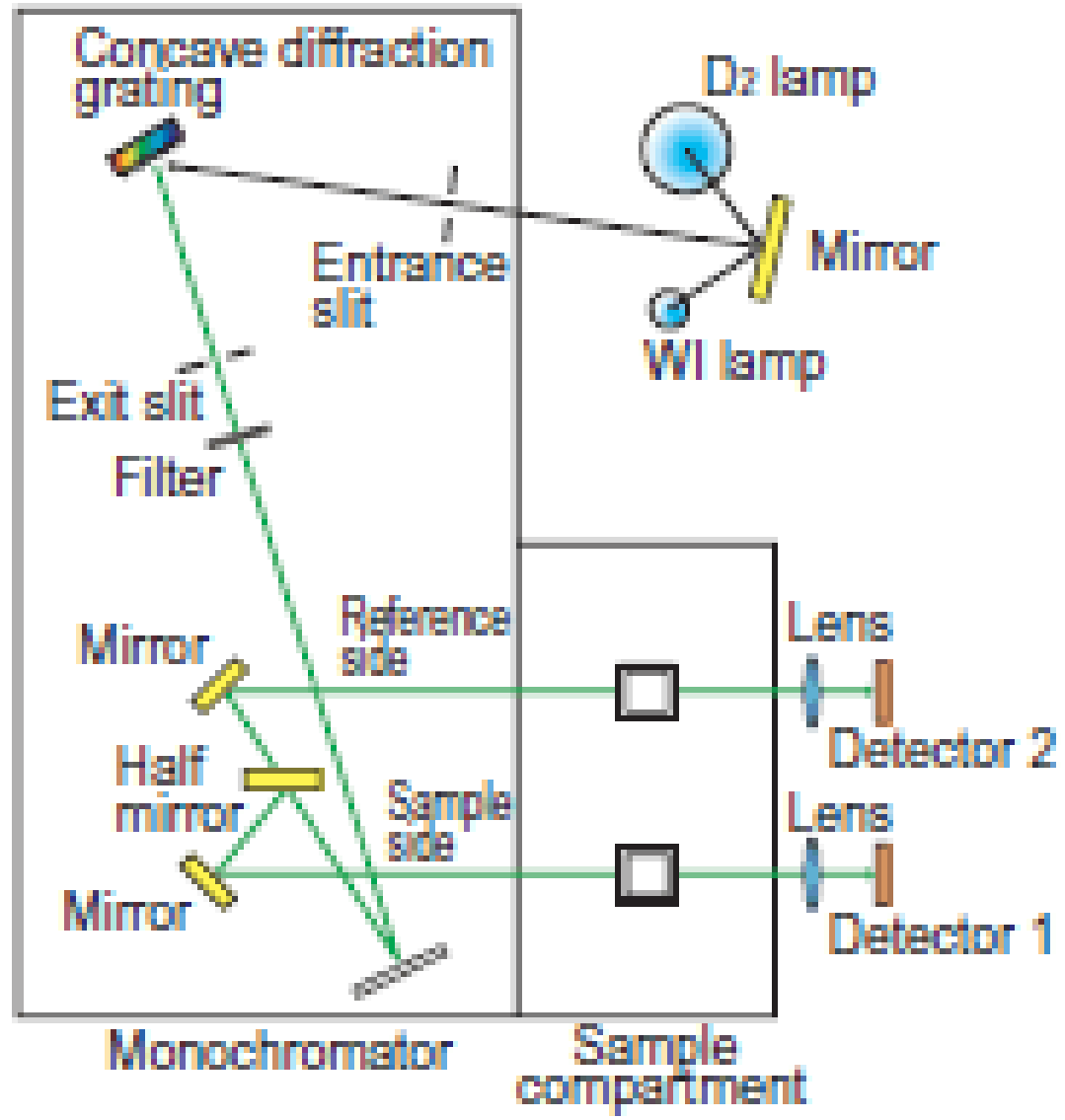


$$m\lambda = d \sin \theta$$

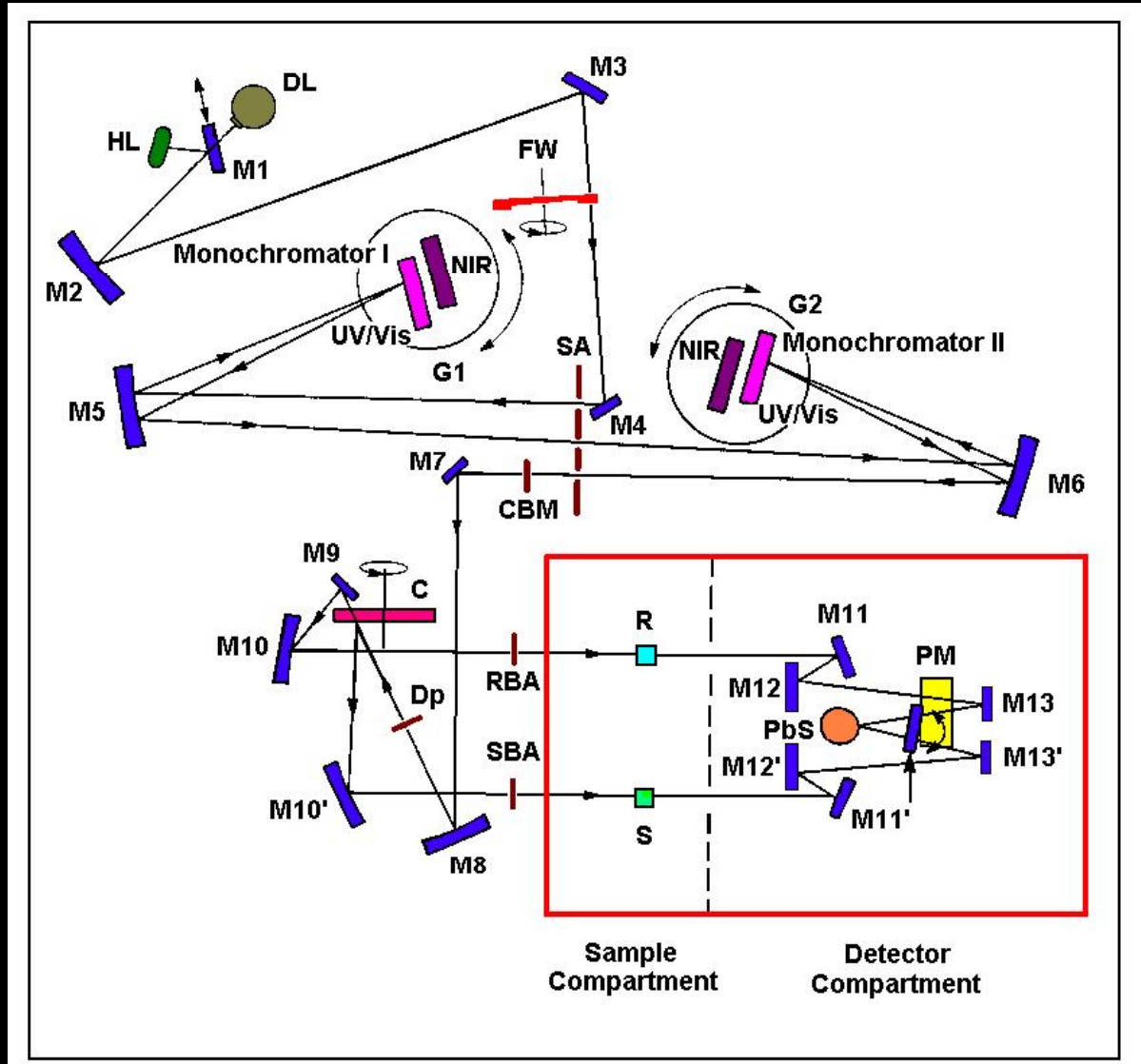


Fatores que influenciam na resolução de um monocromador





Espectrofotômetro Dispersivo



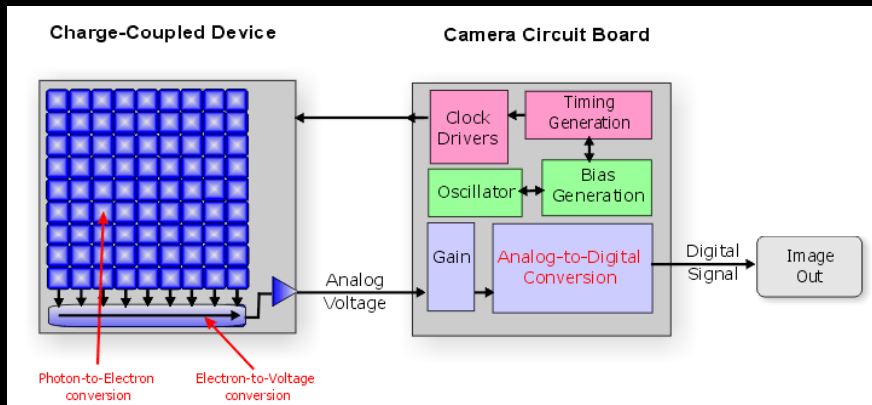
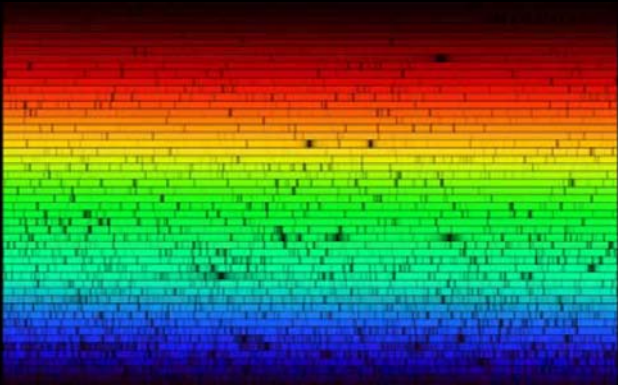
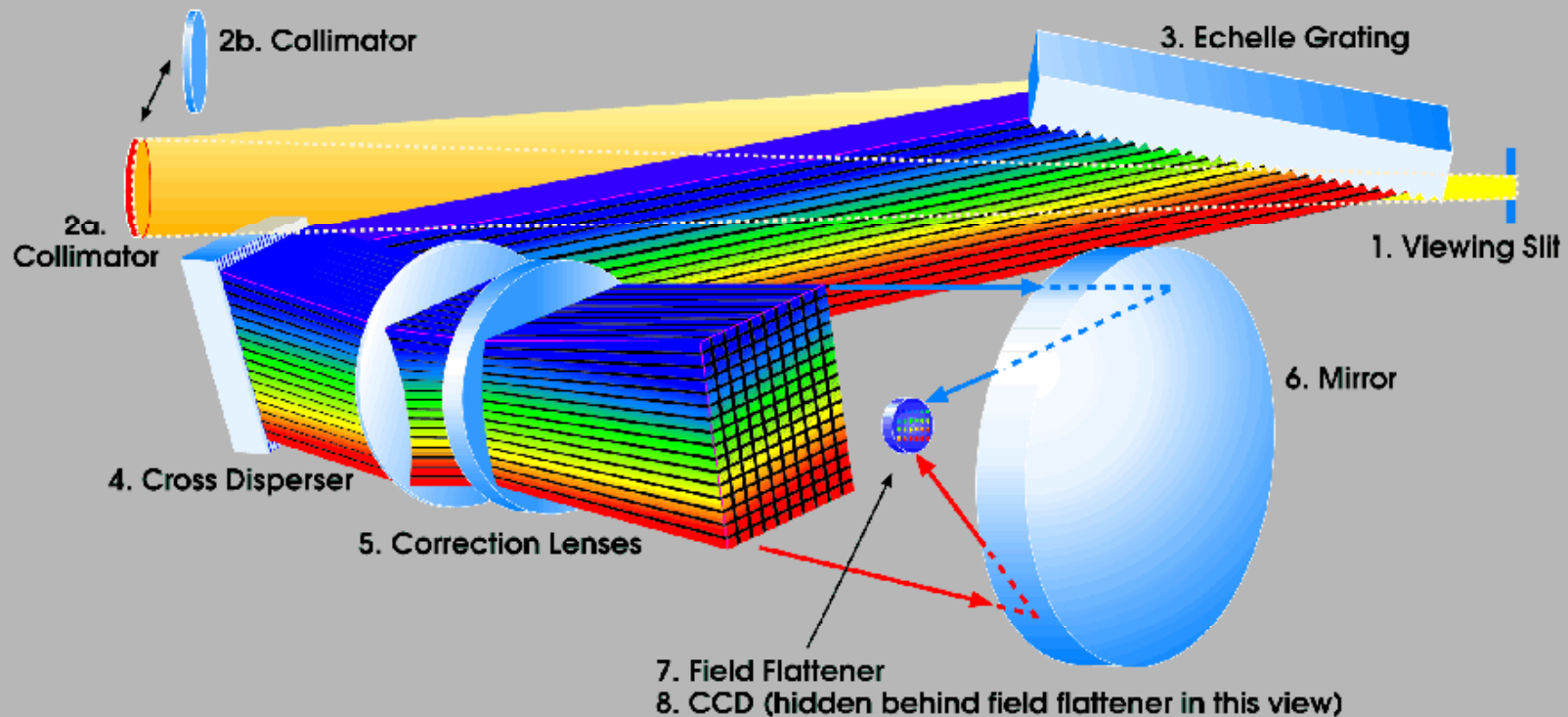
$$I = I_0 e^{-\alpha x}$$



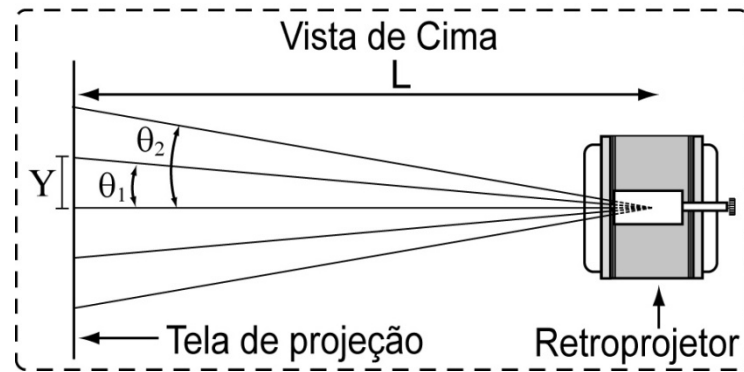
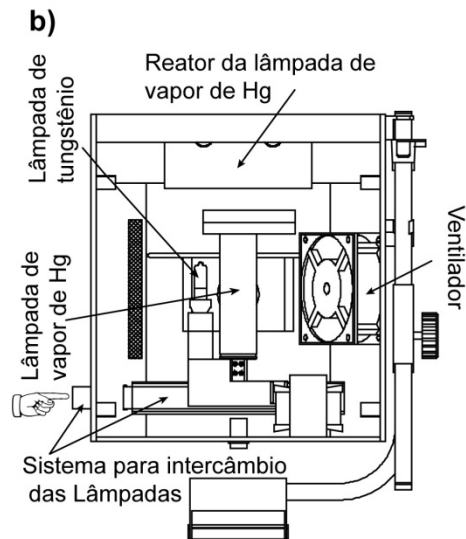
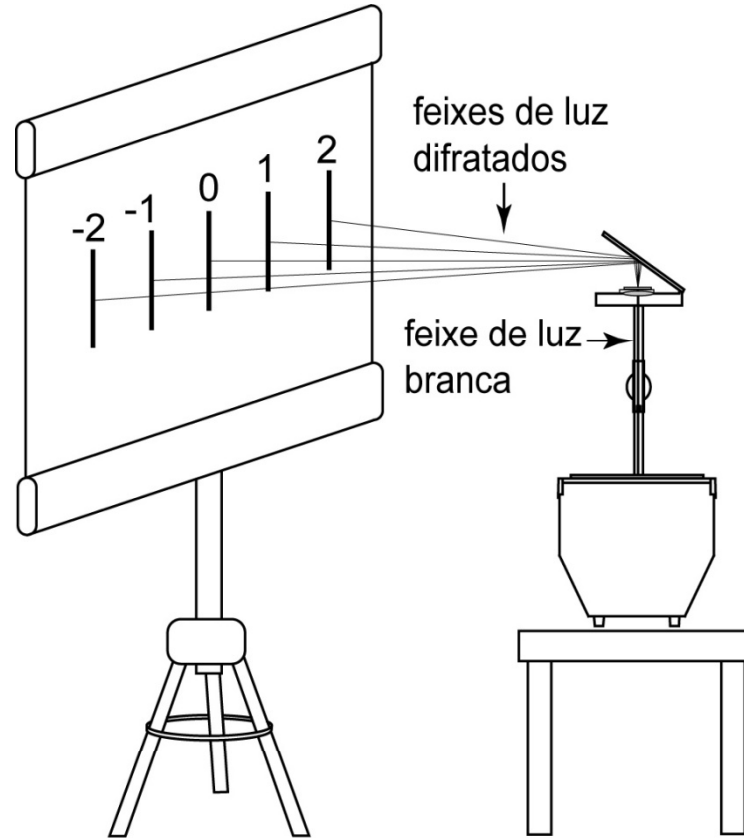
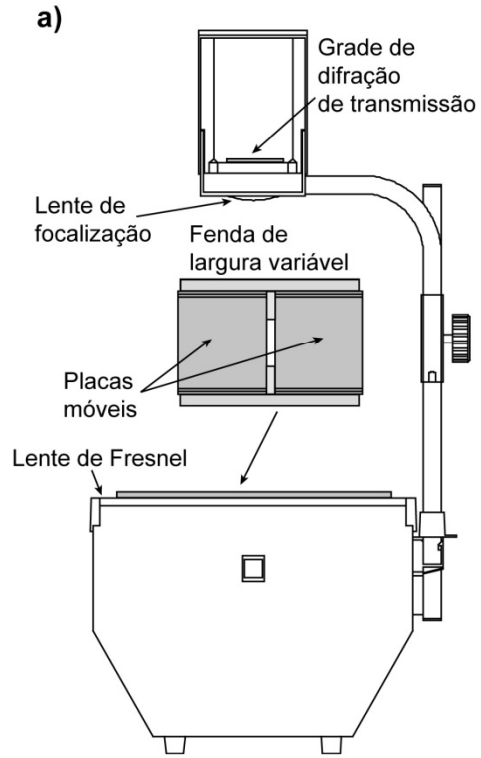
AXSUN
TECHNOLOGY

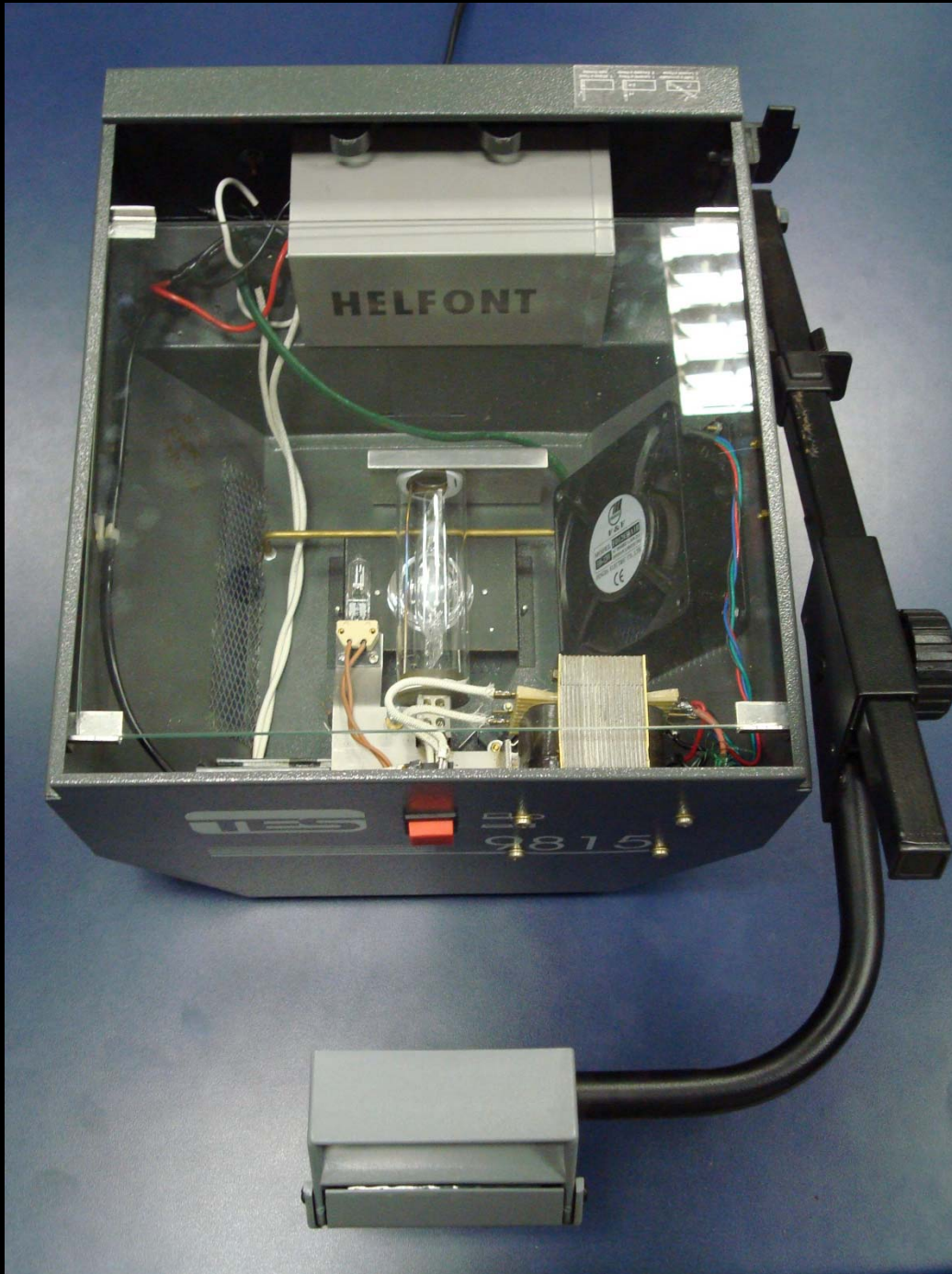


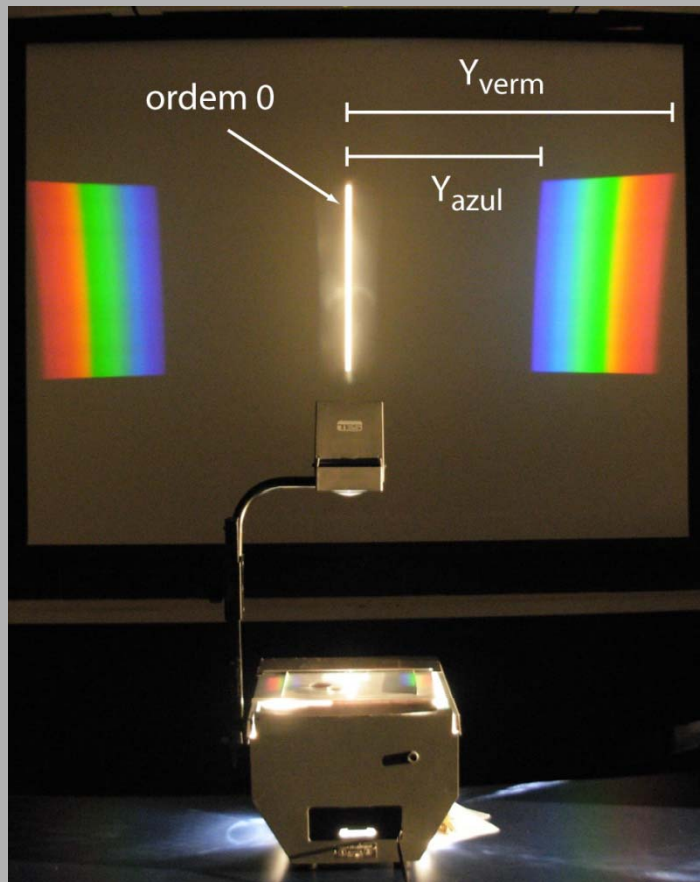
The Light Path of the High-Resolution Echelle Spectrograph



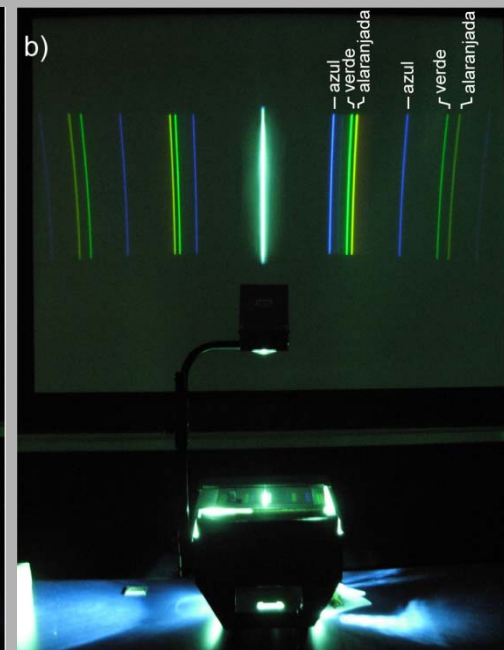
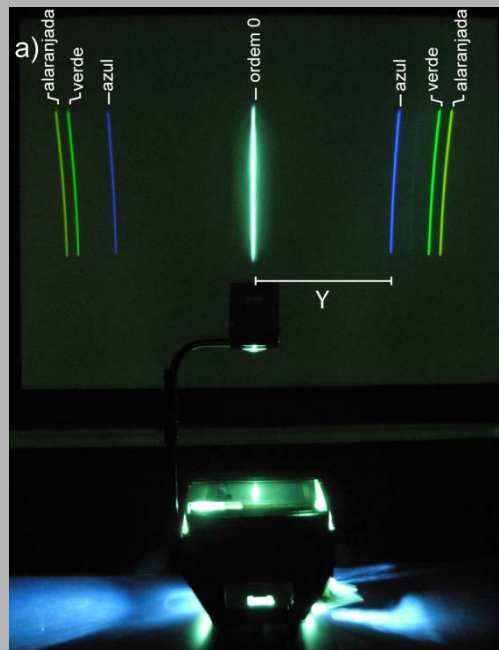




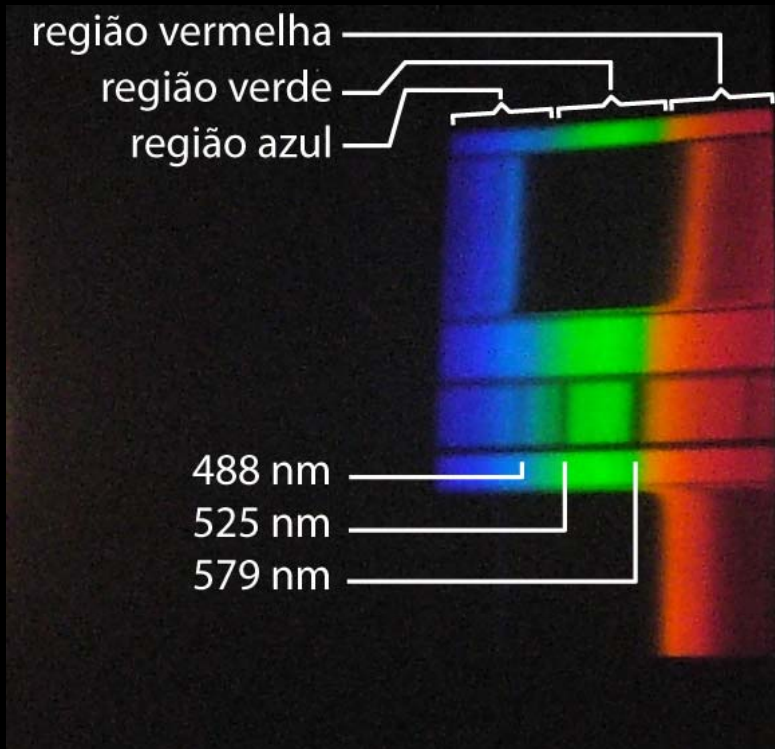
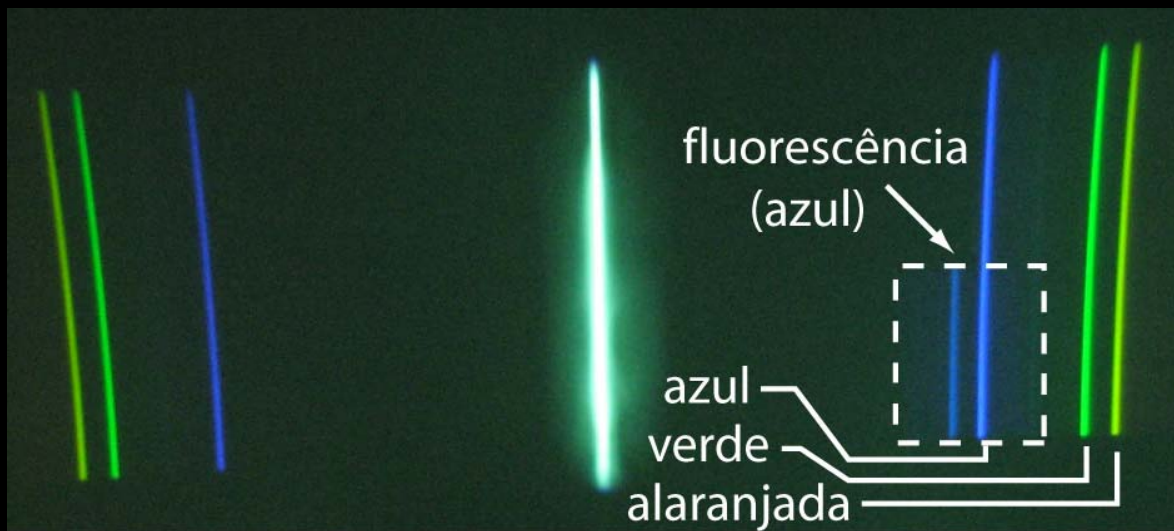




Cor observada	Y (cm)	λ_{medido} (nm)
Início do azul	$Y_{\text{azul}} = 80$	409
Final do Vermelho	$Y_{\text{vermelho}} = 130$	680



Cor observada	Y (cm)	λ_{medido} (nm)	$\lambda_{\text{esperado}}$ ₁₃ (nm)	Erro (%)
amarelo	111,5	581	578,02	0,4
verde	105,0	551	546,07	0,8
azul	82,0	439	435,84	0,8



← filtro 1

← NdCl_3

← filtro 2



Como Fazer Espectroscopia

Analisar a Composição da Radiação

Domínio da Freqüência

Domínio do Tempo

Refração

Difração

Interferência

Ferramenta
Matemática

$$n_1 \text{sen}(\theta_1) = n_2 \text{sen}(\theta_2)$$

$$m\lambda = d \text{sen}(\theta)$$

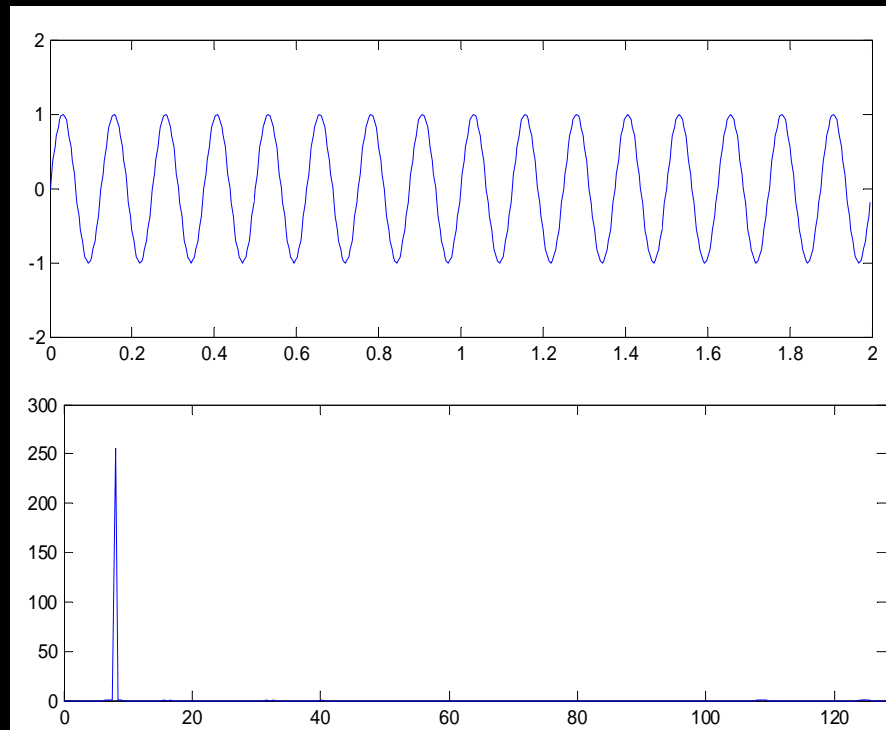
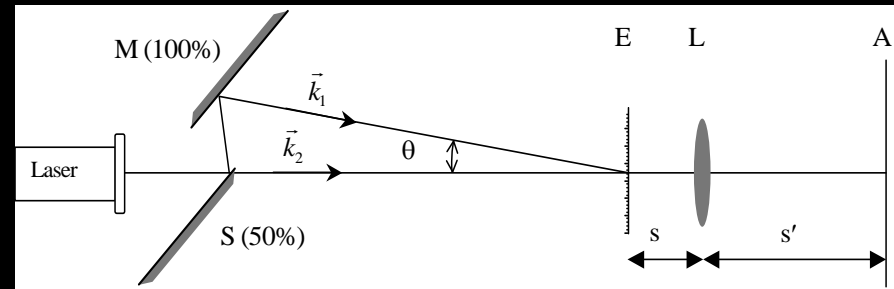
Interferência



Jean Baptiste Joseph Fourier



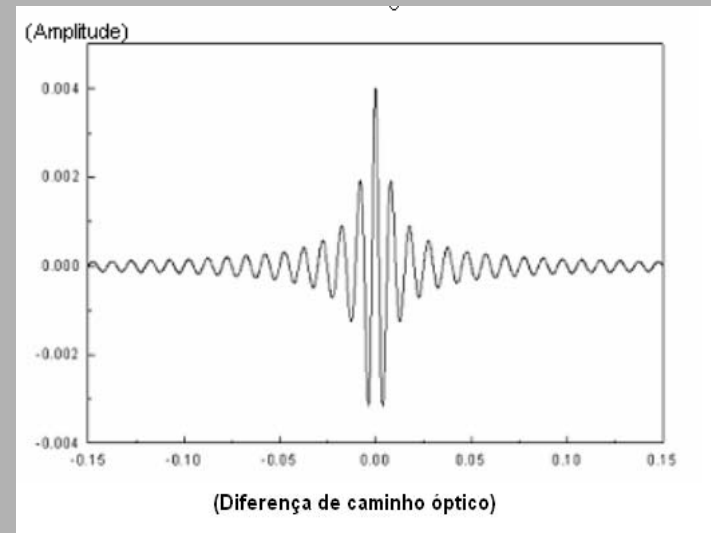
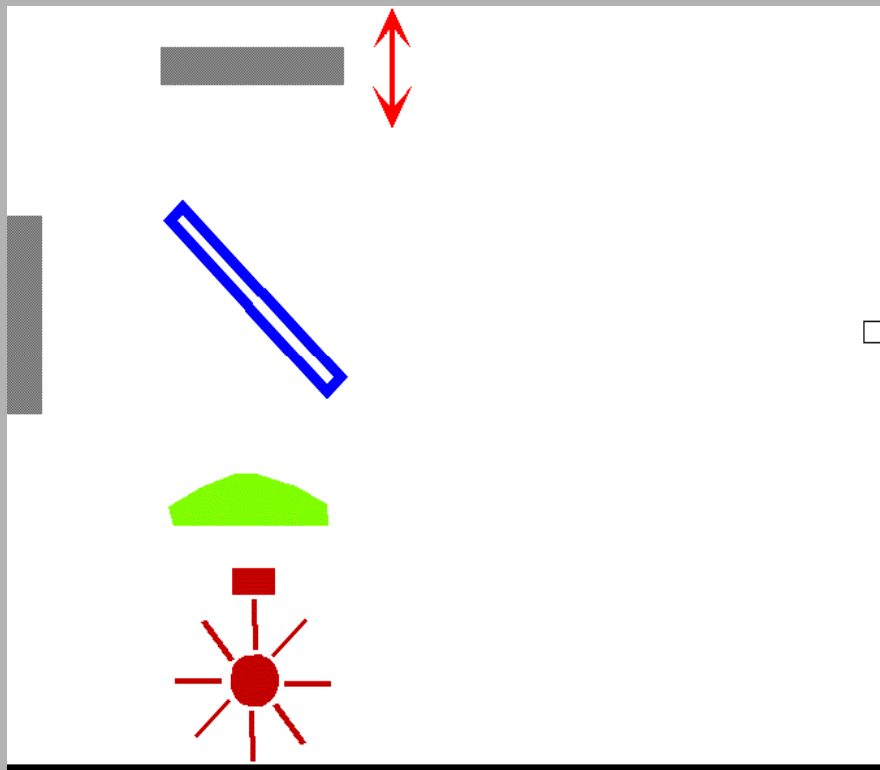
Johann Carl Friedrich Gauss
(1777 – 1855)

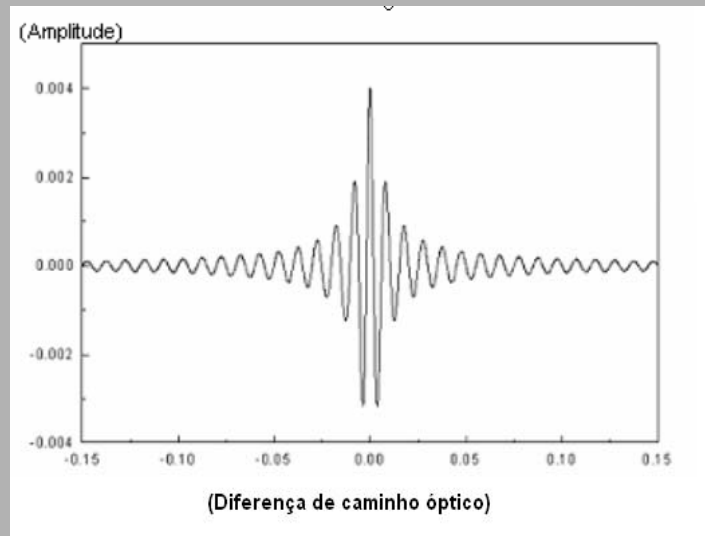


J.W. Colley e J.W. Tukey
1065 Algoritmo para calculo
Rapido FT \Rightarrow **FFT**

Espectroscopia no Espaço do Tempo

Interferência





Jean Baptiste Joseph Fourier

$$I(\delta) = \int_{-\infty}^{\infty} B(\nu) \cos(2\pi\delta / \lambda) d\nu$$

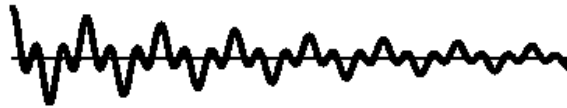
$$I(\delta) = \frac{a_0}{2} + \sum_{k=1}^{\infty} \left(a_k \cos(kx) + b_k \sin(kx) \right)$$

$$I(t) = \frac{a_0}{2} + \sum_{k=1}^{\infty} \left(a_k \cos(k \nu t) + b_k \sin(k \nu t) \right)$$

- *Algoritmo para o cálculo dos coeficientes a_k, b_k*
- *Apenas Soma e Multiplicação*
- *Critérios de Apodização*

Por que transformada de Fourier é tão importante?

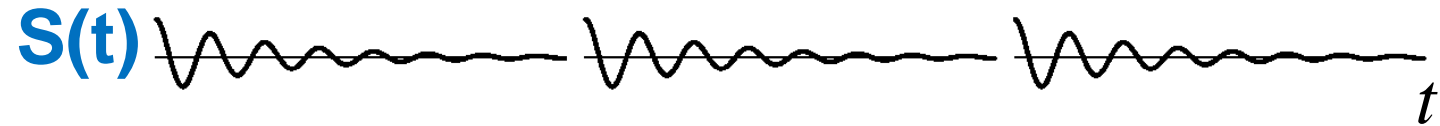
- O sinal detectado em espectroscopia de RMN está no domínio do tempo. Esta é uma diferença importante em relação a outros tipos de espectroscopias e é talvez umas das razões principais do poder da RMN.



- É praticamente impossível fazer a discriminação de “quantas” frequências estão em um sinal no domínio do tempo se mais de três frequências estão presentes .

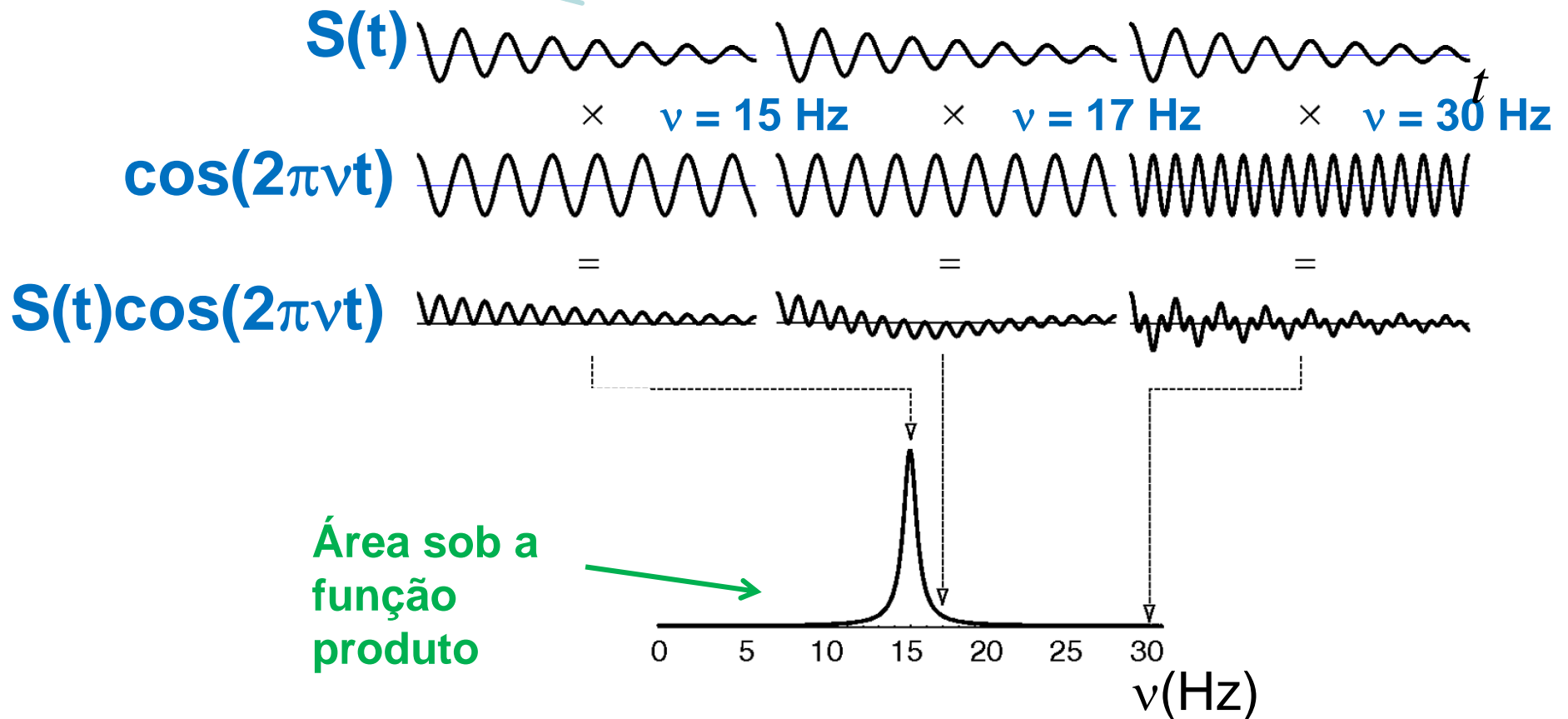
Em outras palavras. Sem a transformada de Fourier não existiria espectroscopia de RMN.

Sobre um significado transformada de Fourier

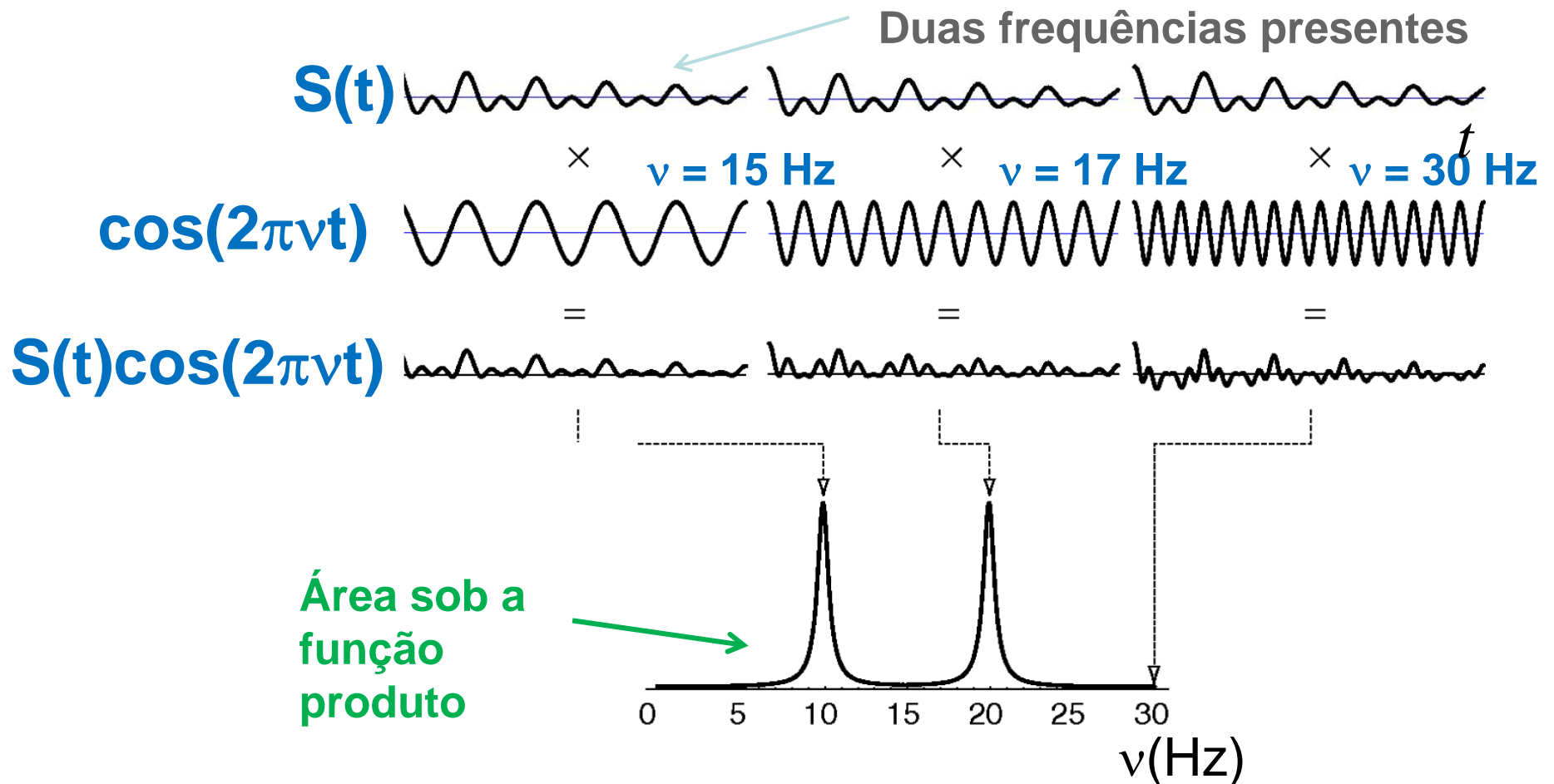


Sobre um significado transformada de Fourier

decaimento mais lento



Sobre um significado transformada de Fourier



Pergunta : Faria diferença se ao invés da função cosseno fizéssemos a análise com uma função seno?

Definição da transformada de Fourier

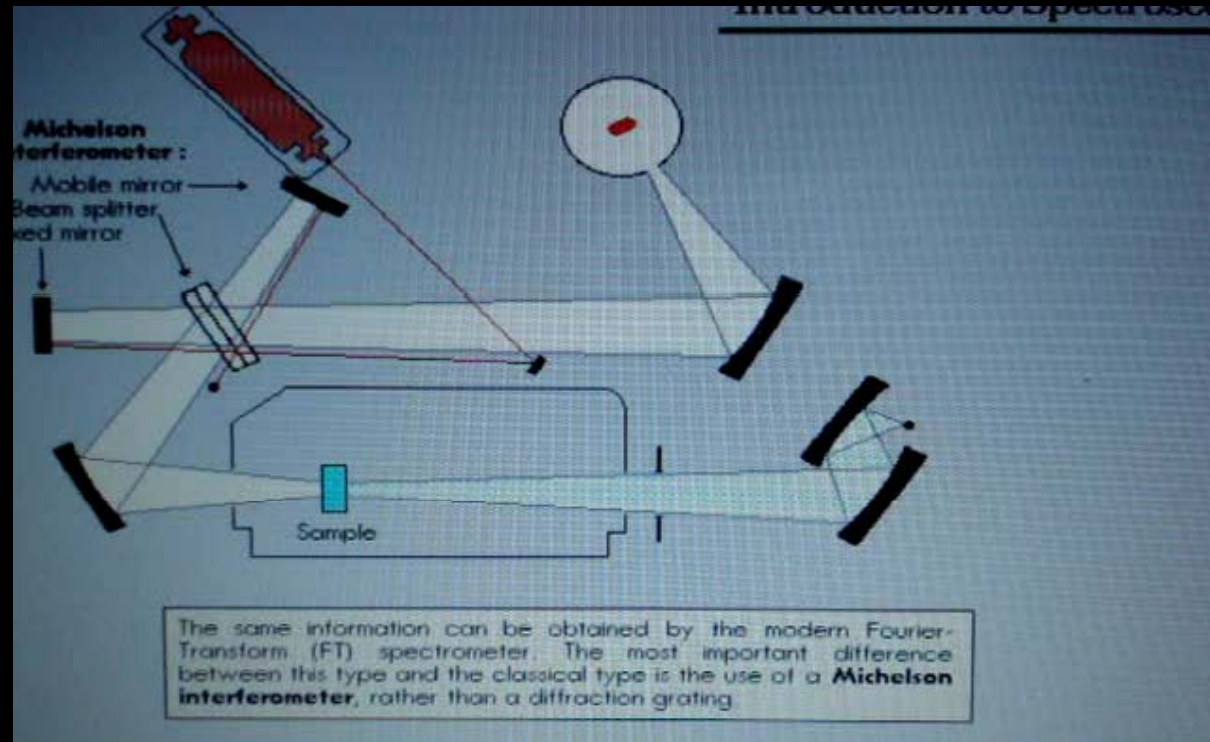
Como $e^{i\omega t} = \cos(\omega t) + i \sin(\omega t)$, podemos então generalizar o procedimento para o plano complexo fazendo:

$$S(\omega) = \int_0^{\infty} \overbrace{S(t)e^{-i\omega t}}^{\text{produto}} dt$$

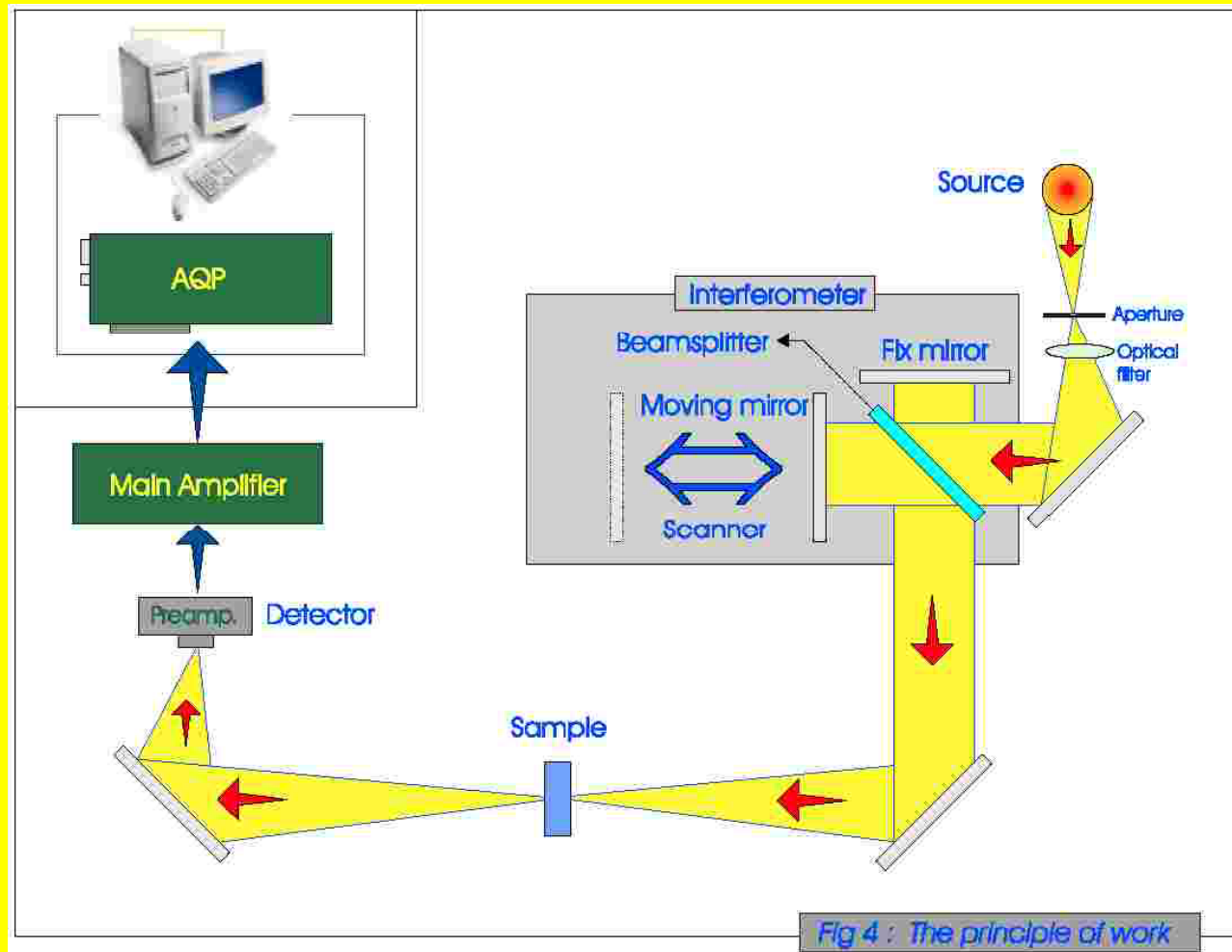
Área

$$S(\nu) = \int_0^{\infty} S(t)e^{-i2\pi\nu t} dt$$

Transformada de Fourier:
Permite discriminar quais as
componentes de frequência de
 $S(t)$.

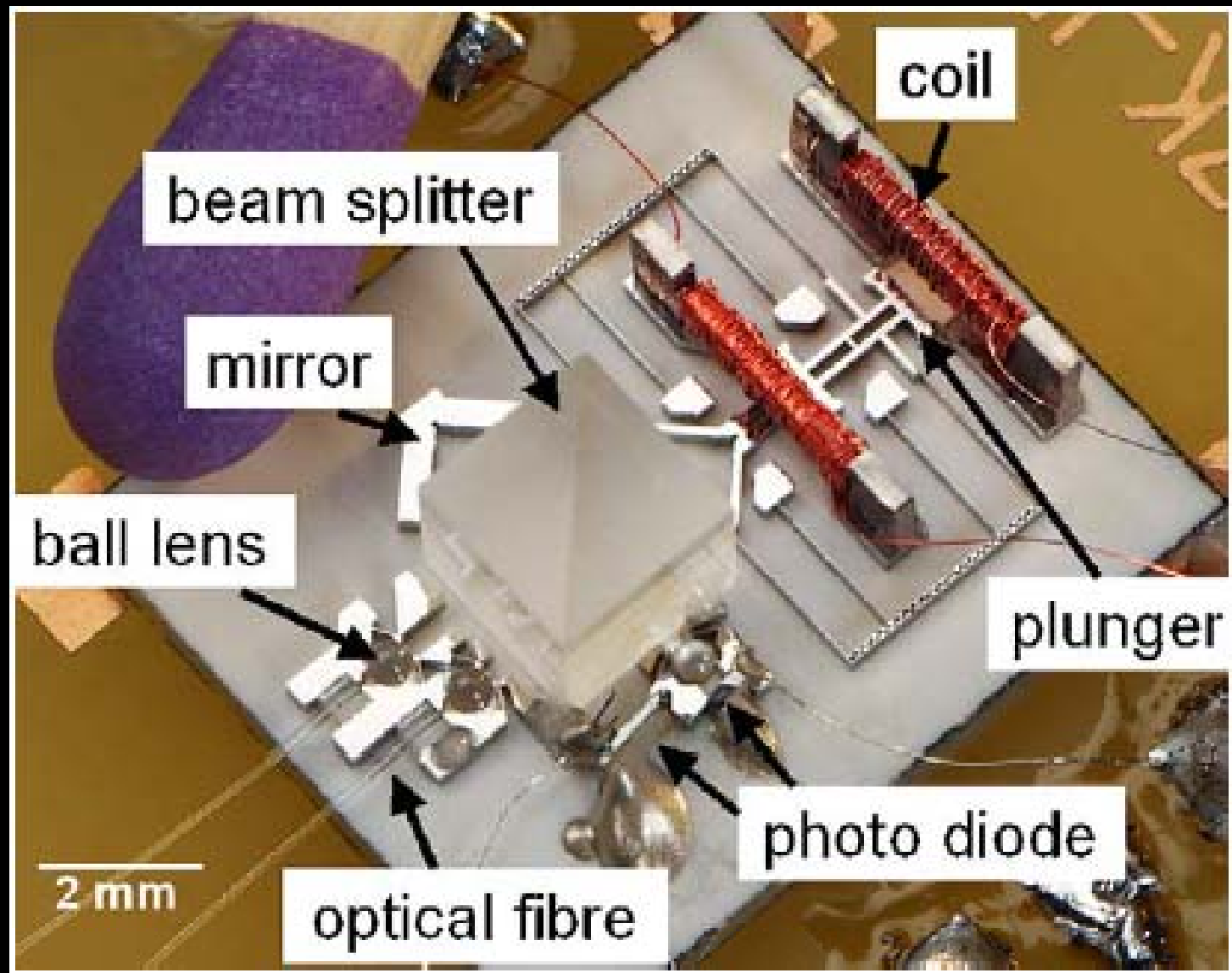


The same information can be obtained by the modern Fourier-Transform (FT) spectrometer. The most important difference between this type and the classical type is the use of a **Michelson interferometer**, rather than a diffraction grating.

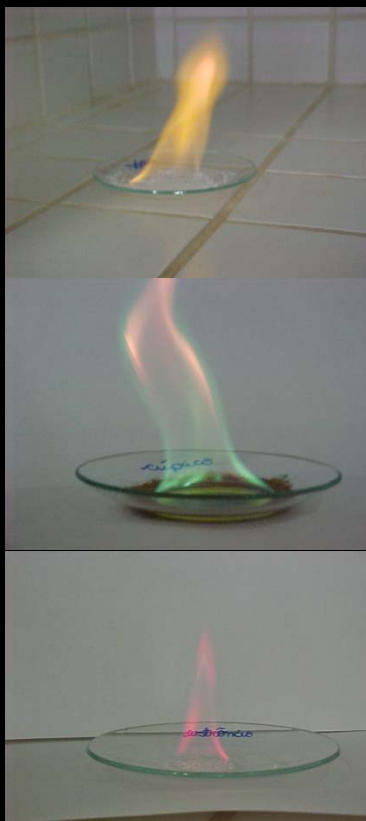


Vantagem de Jaquinot – não há fendas
Vantagem de Fellgett - varredura única





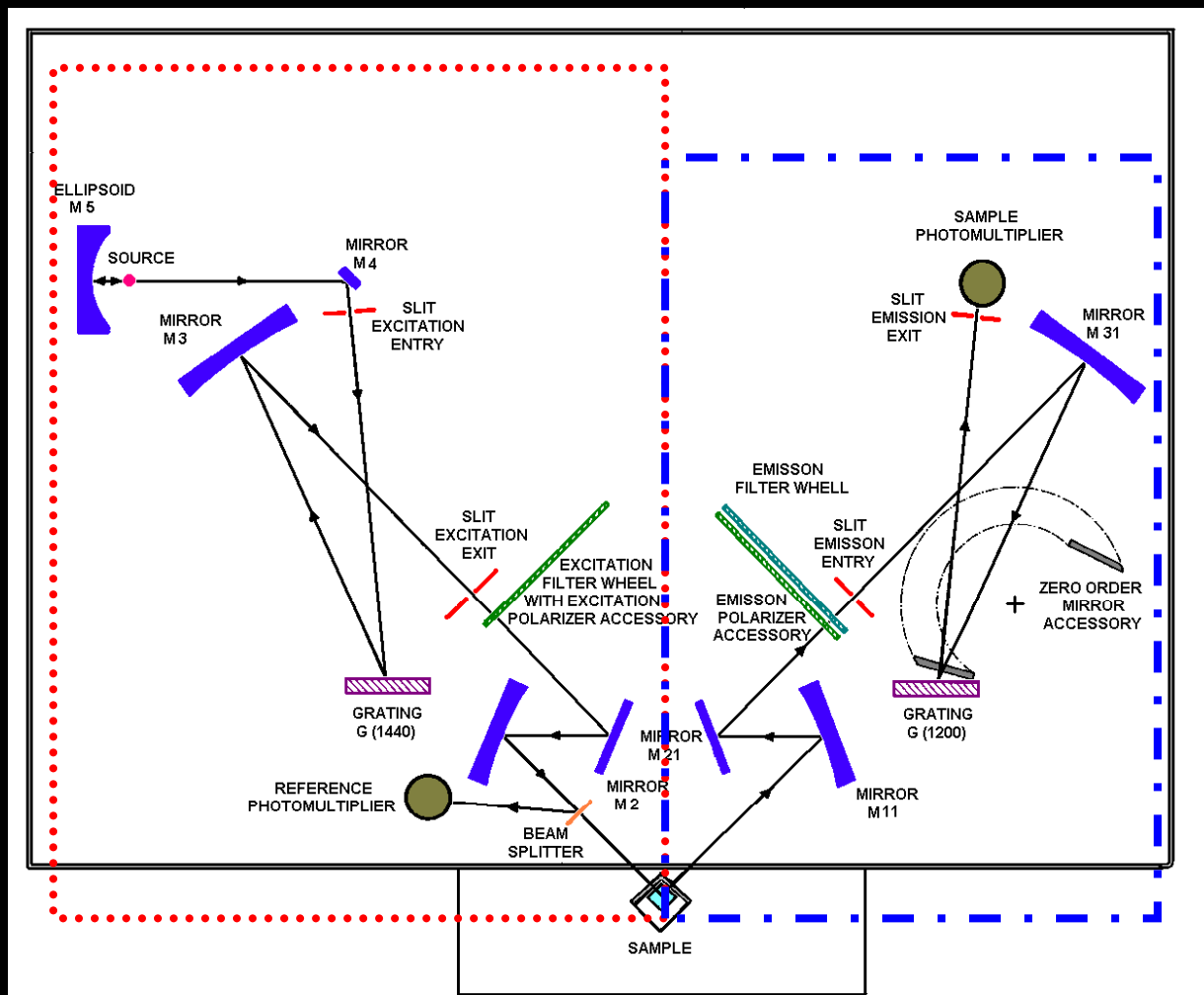
Fluorescência



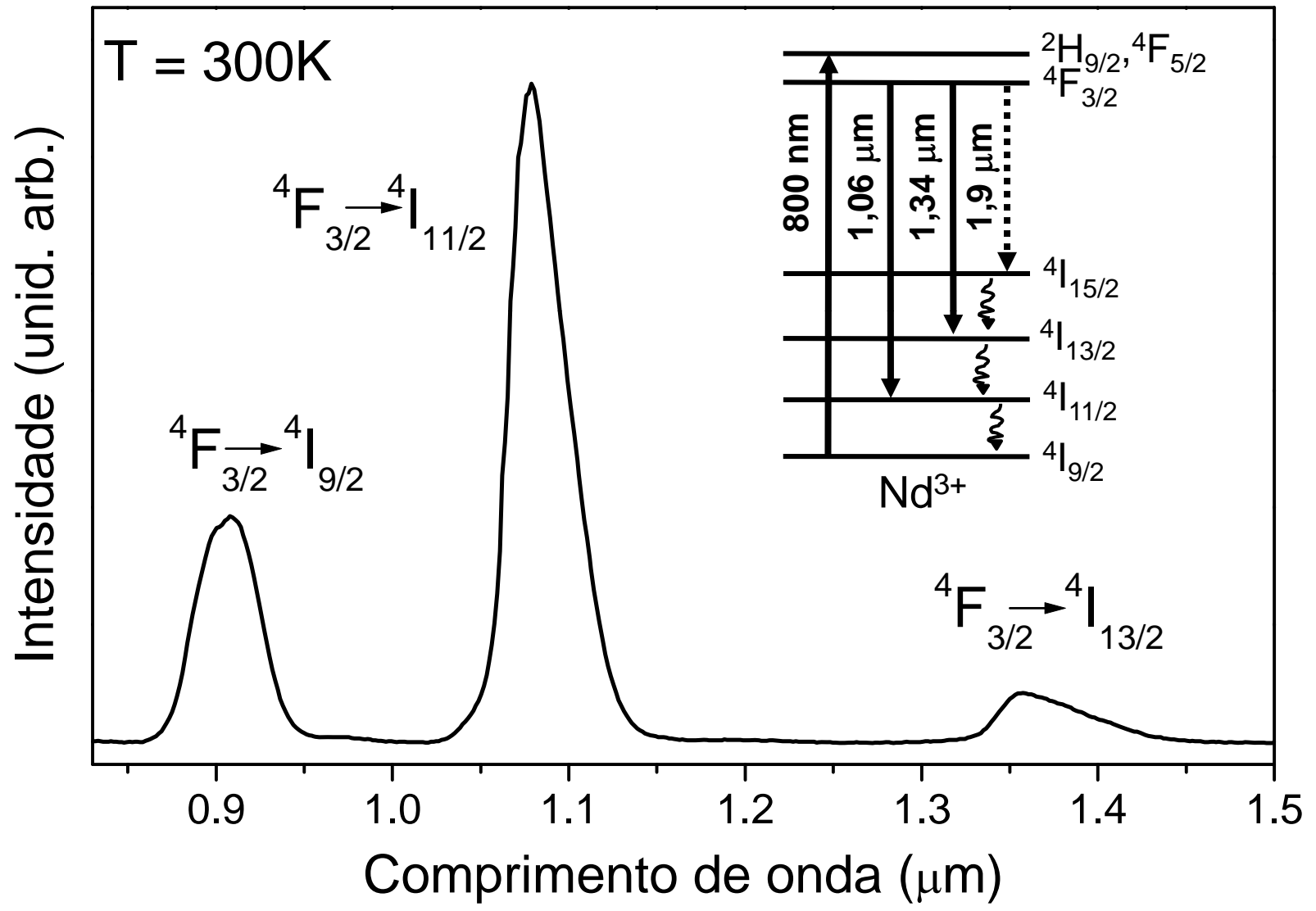
Sódio

Cobre

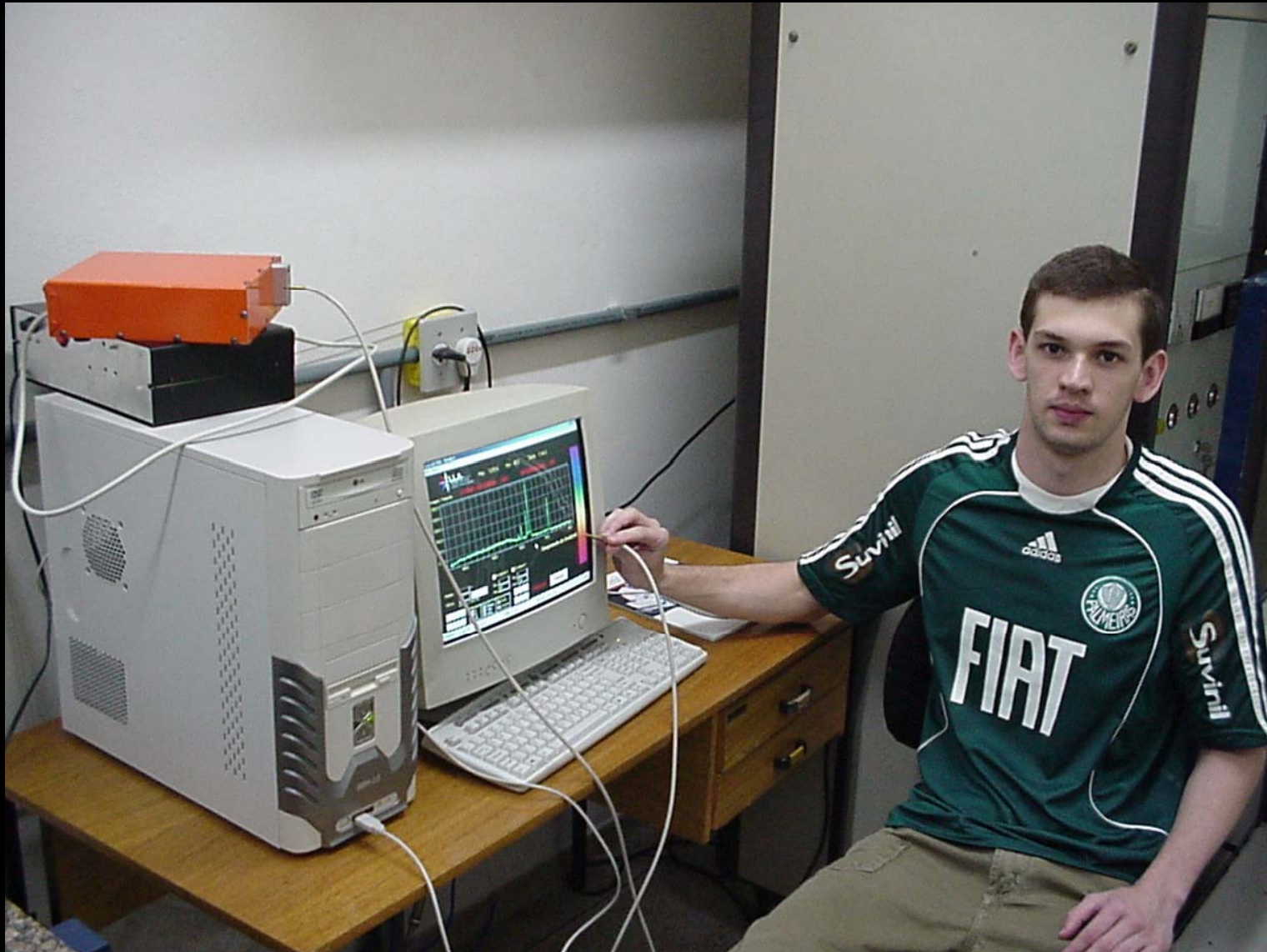
Estrôncio

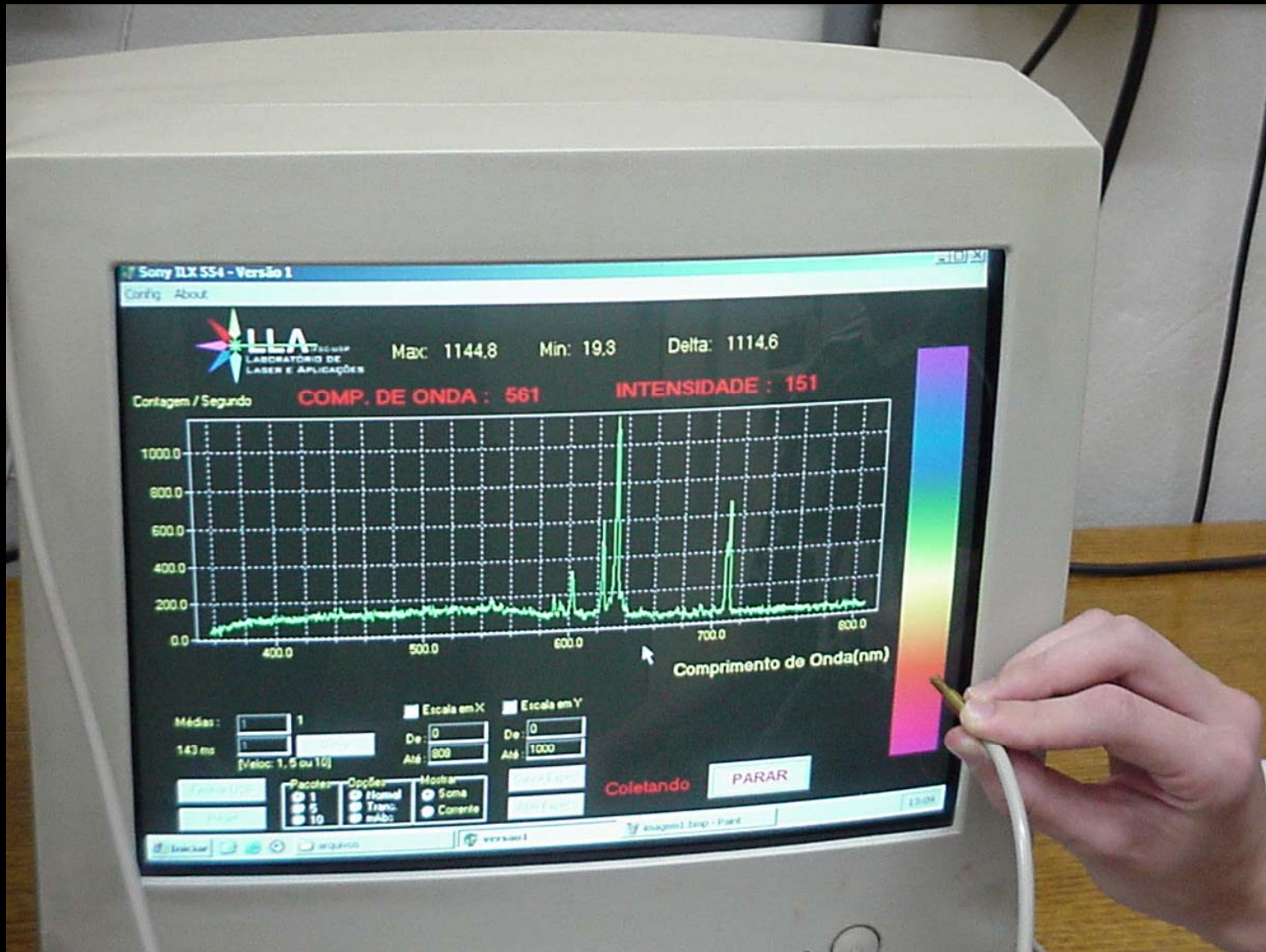


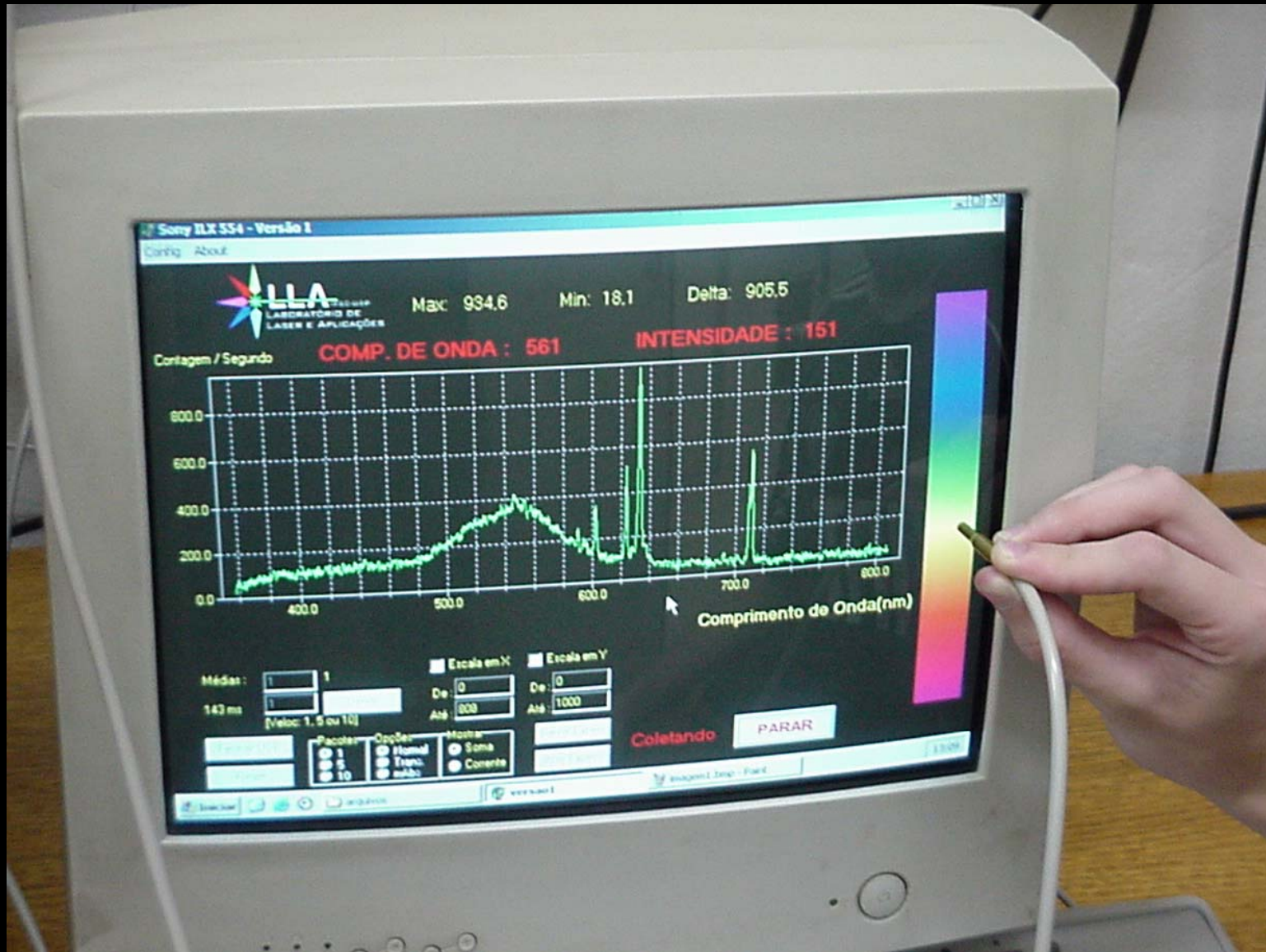
Luminescência de GaLaS:Nd³⁺

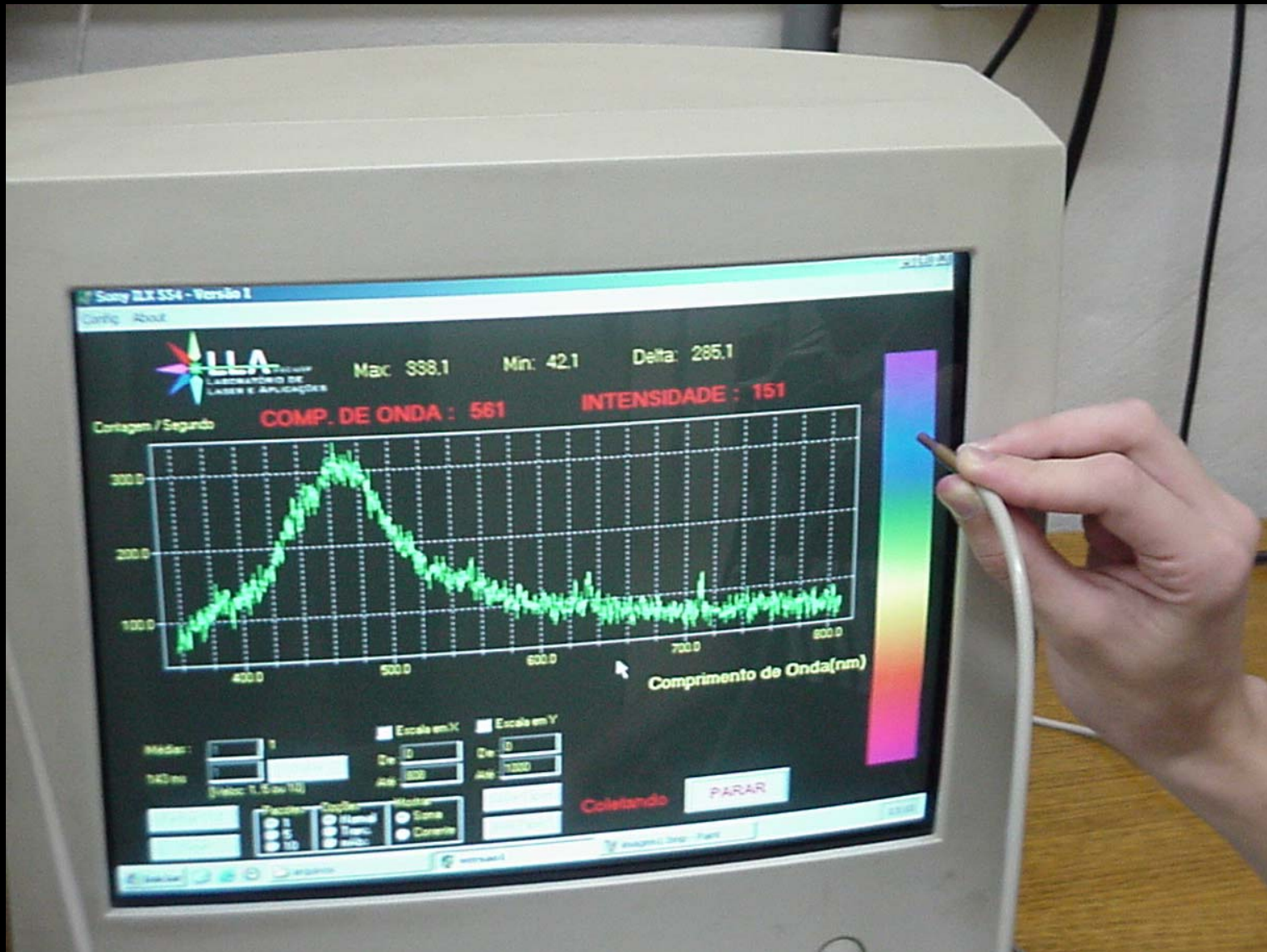


CCD Sony ILX 554











Aplicações

Detecção de Poluentes na Atmosfera

Absorção Óptica Diferencial

DOAS

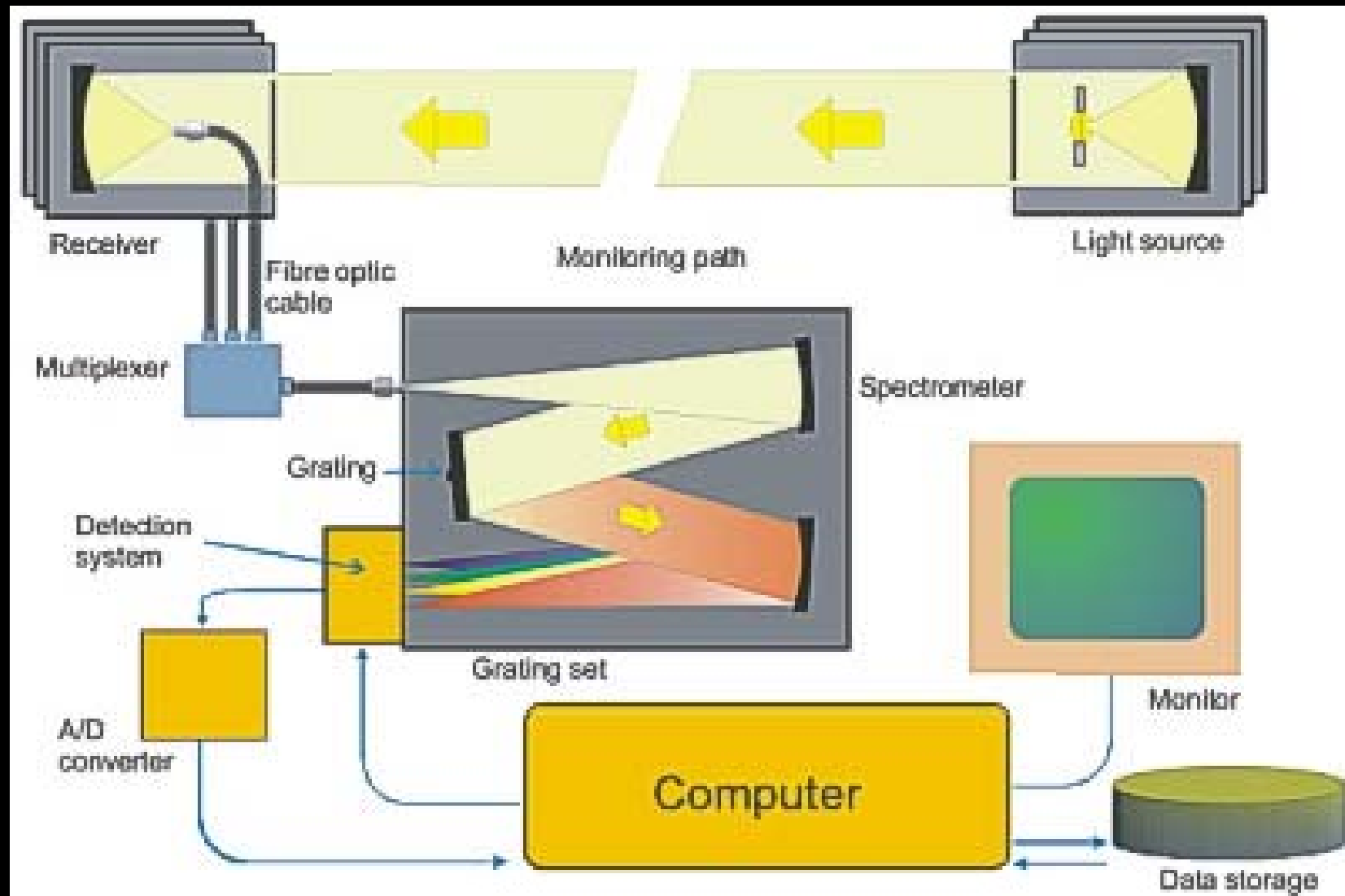
Parte por Bilhão
Parte por Trilhão

$$I = I_0 e^{-\alpha x}$$

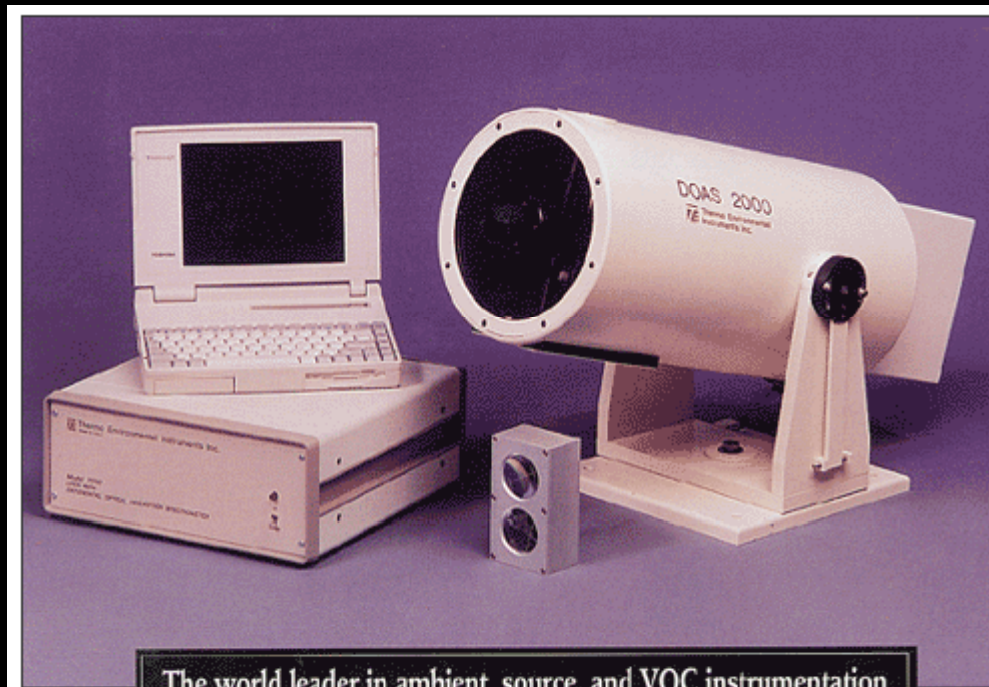
Vantagens da Técnica

- Sensibilidade (ppt) e Precisão (1-10 %).
- Boa Especificidade.
- Monitoramento Remoto + Tempo Real
- Portátil
- Fácil Construção

Absorção Óptica Diferencial (DOAS)

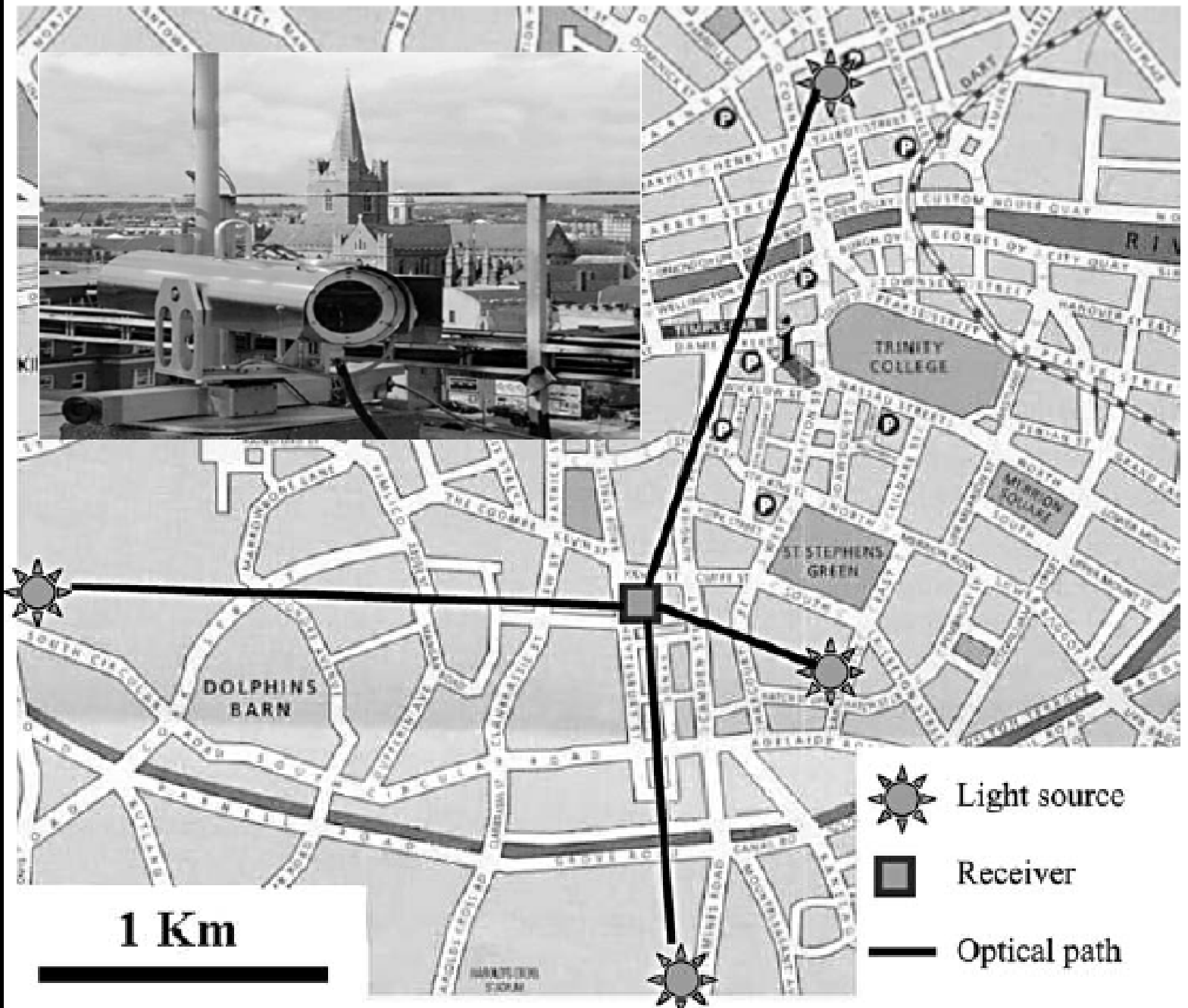


$$I = I_0 e^{-\alpha L}$$






The world leader in ambient, source, and VOC instrumentation presents the world's finest long-path monitoring system.

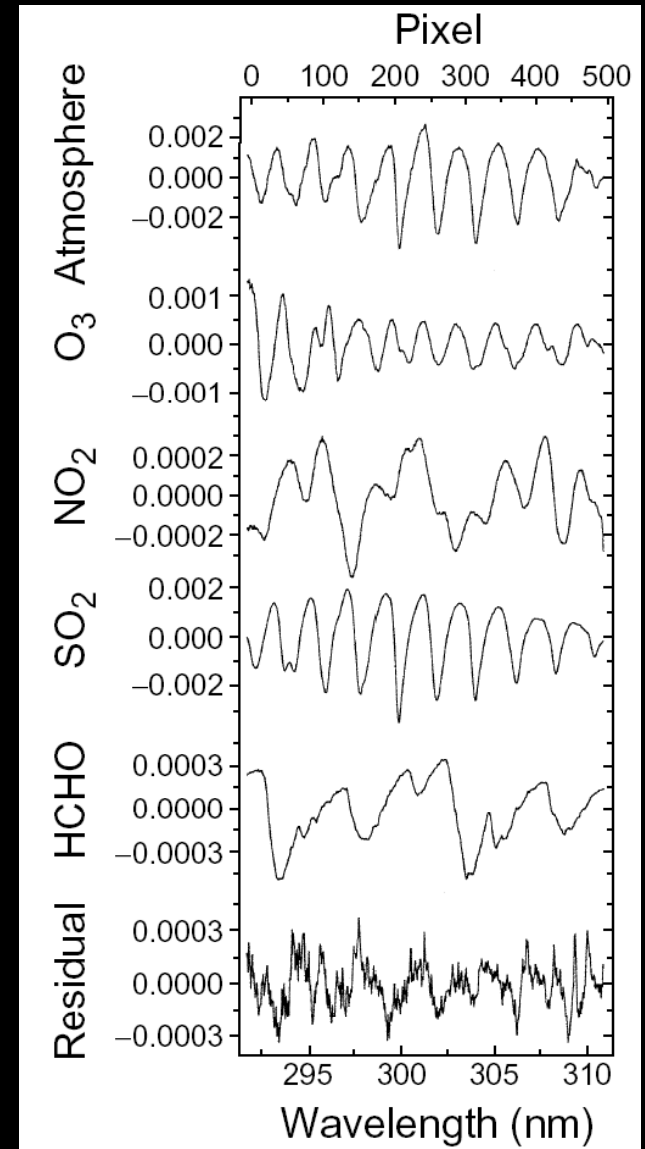
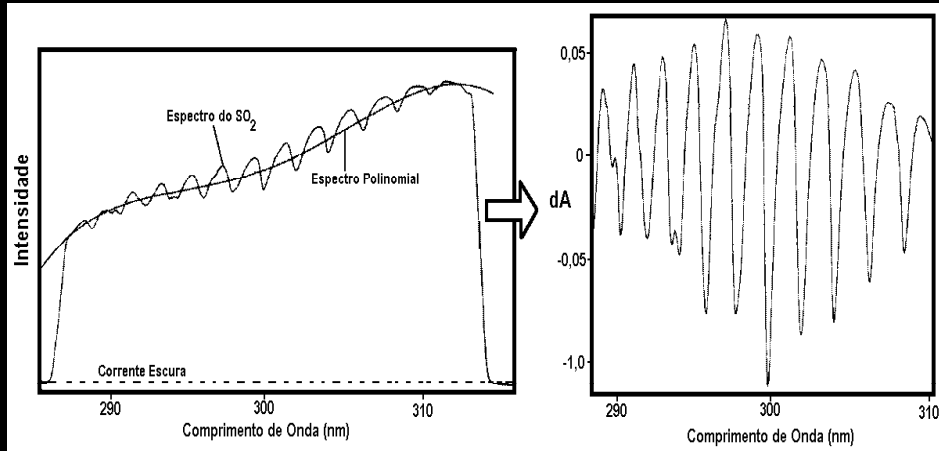




1 Km

-  Light source
-  Receiver
-  Optical path

Princípio da Técnica DOAS



ProgDOAS_MC CCD - Sistema de Espectroscopia por Absorção Diferencial

Arquivo Edição Dados Aquisição Matemática Opções Configurações Ajuda

Planilha de Aquisição de Dados

Lim. do Ajuste
 Canal Ini 70
 Canal Fin 1023

Lim. Numéricos
 Canal Ini 1
 Canal Fin 1024

Parâmetros da Varredura
 N. Pontos Exp. 1024
 N. Varreduras 1000
 Tempo de int. (μs): 215

Simples Inverter Sinal
 Contínua Sob. Espectros

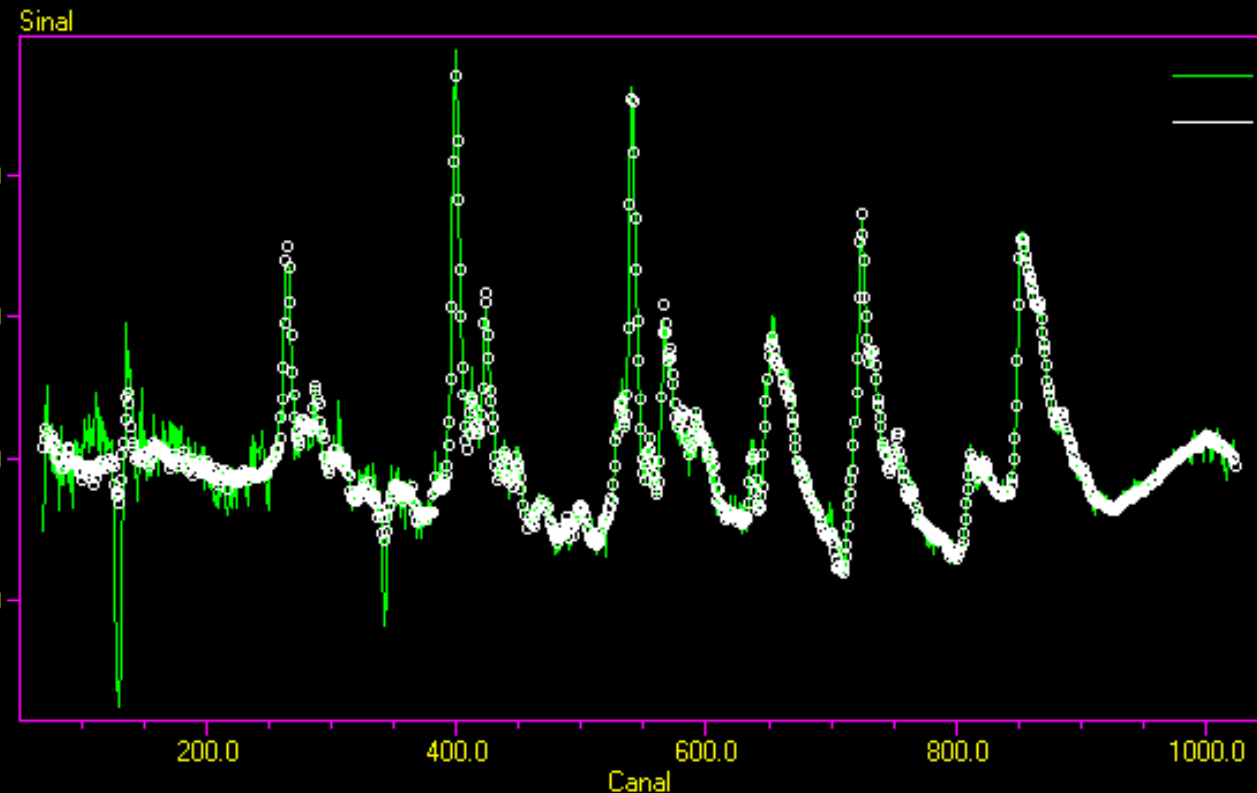
Resultados

Espécie	Concentraç	
BENZENO	0.129	0
M-XILENO	0.122	0
O-XILENO	0.139	0
P-XILENO	0.0908	0
TOLUENO	0.098	0

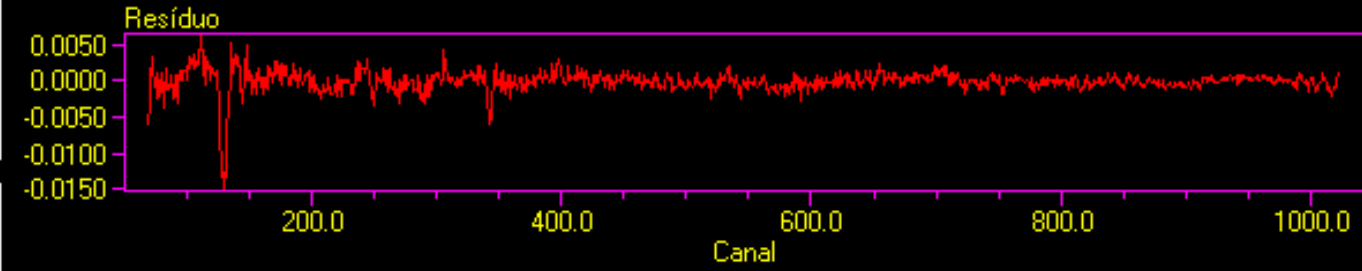
RMS= 32.69 % Res. = 2.1E-2
 Chisq= 2.232E-3

O-XILENO 17-02-2007= 1.3850E-1
 P-XILENO 17-02-2007= 9.0762E-2
 TOLUENO 17-02-2007= 9.7966E-2

Transmissão Serial/USB
 Tx Rx Conectado
 19231

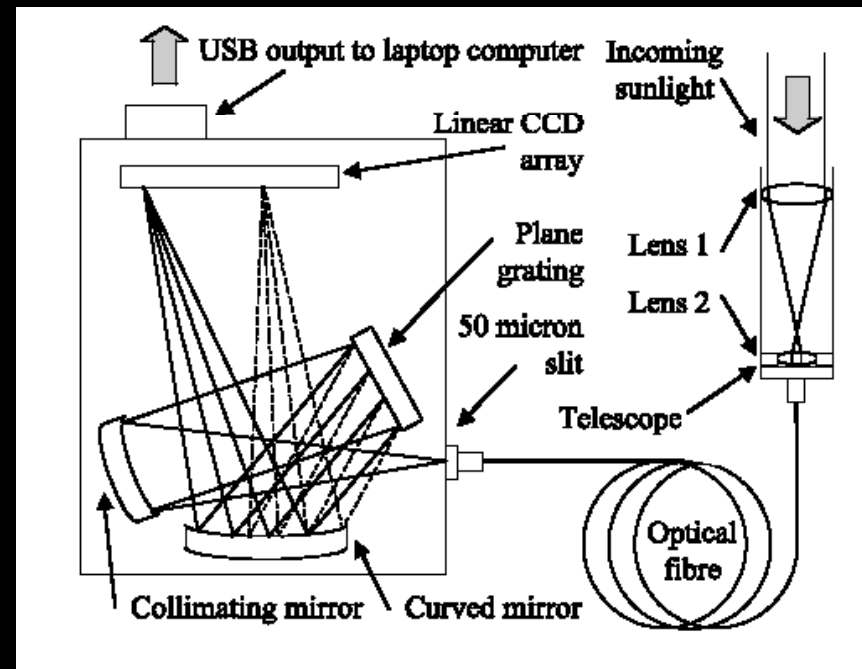


Posição: $x = 621.2$ $y = -1.419E-3$ $\Delta Y = 626.7 \text{ u.b.}$ $Y_m = 2.1214E+2 \text{ u.b.}$

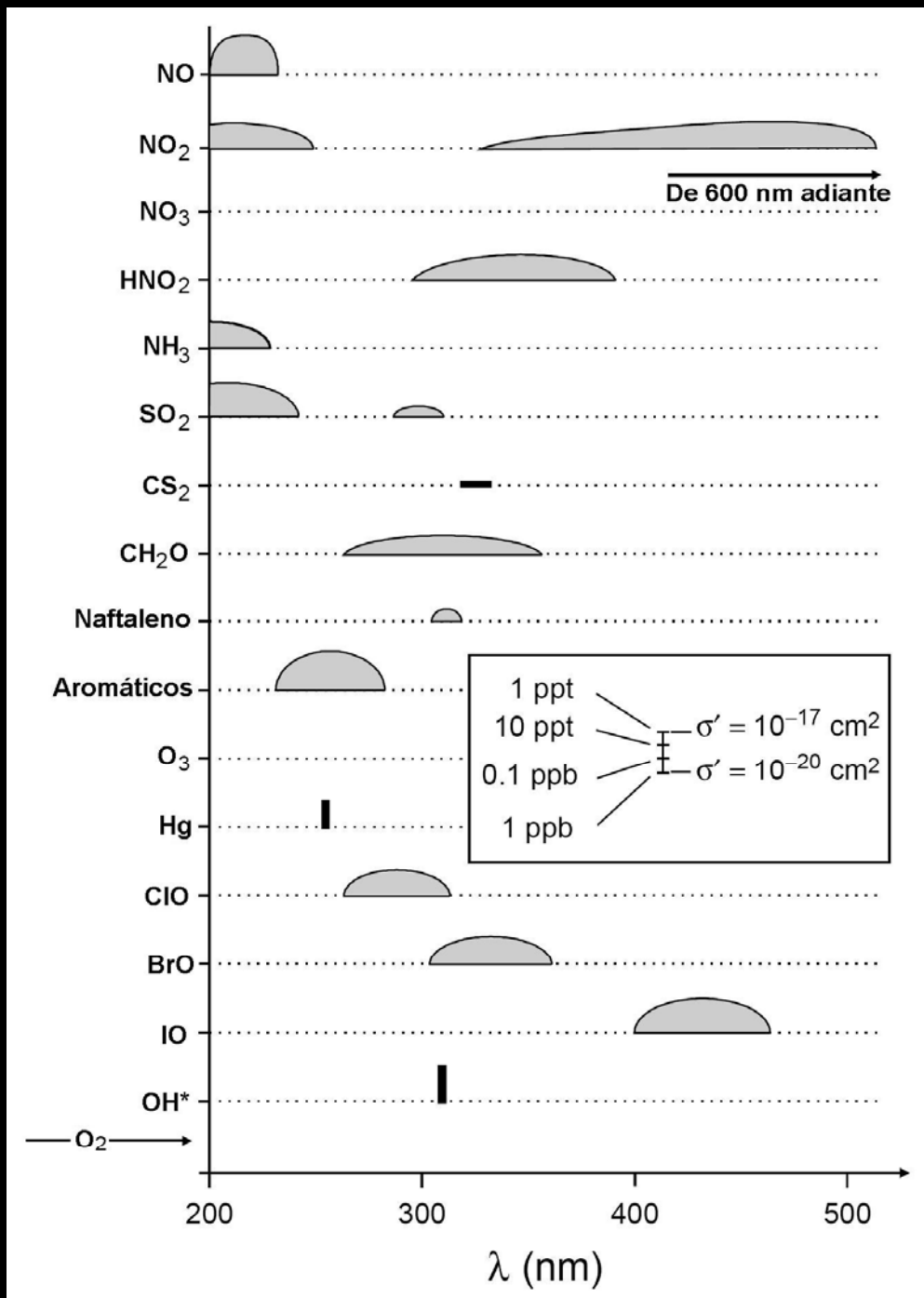


Dispositivo Pronto

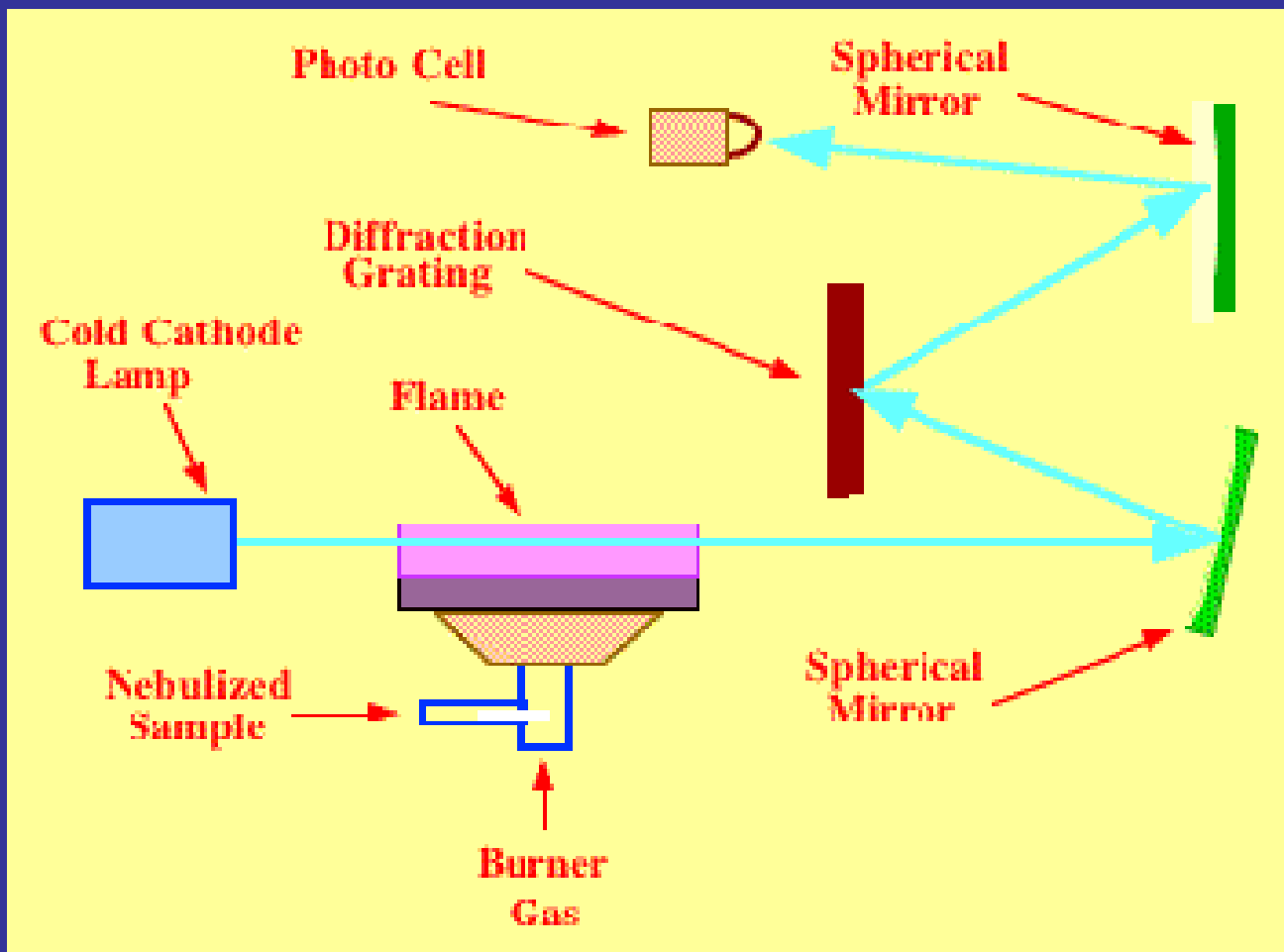
Baud=19231



Substâncias Detectadas

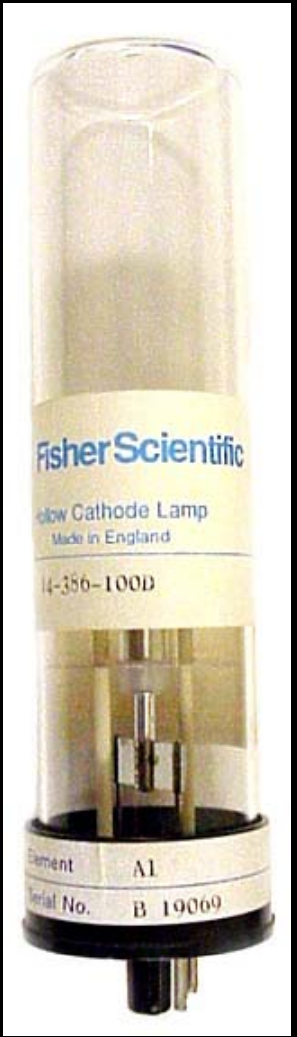
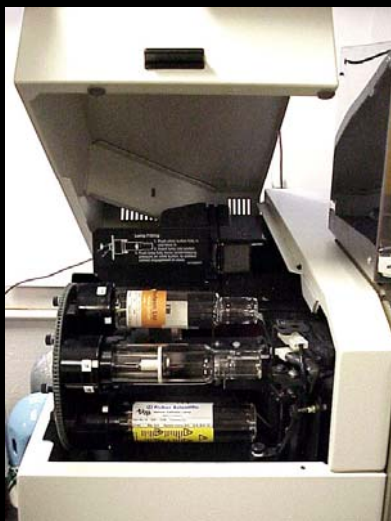


Espectroscopia de Absorção Atômica



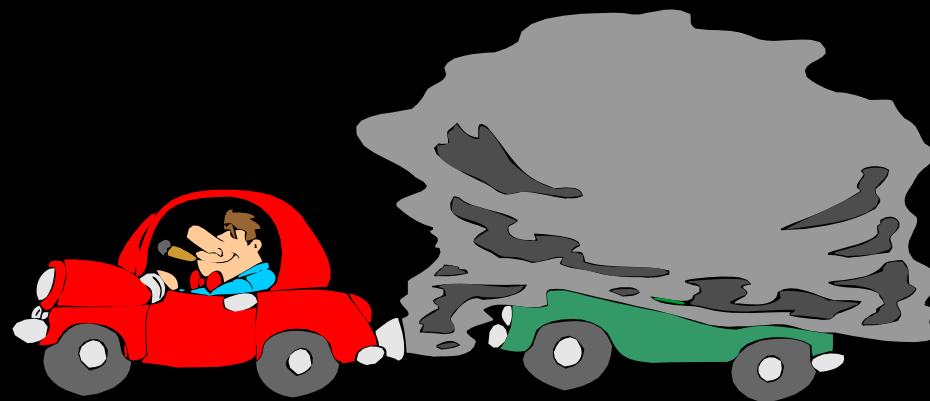
Alan Walsh 1950-1960





Análise de Gases

Exaustão Automotiva



CO NO_x HC

CO₂

O₂

CO (%vol)

- **Monóxido de Carbono**
- **Resulta de uma combustão incompleta**
- **Instável e muito tóxico**
- **O CO deveria ser um CO₂, porém, na falta de O₂ (mistura rica) o Carbono(C) combina-se na queima apenas com um oxigénio (O), quando o ideal seria combinar-se com dois**
- **Menor percentagem de CO => melhor Combustão**

HC (ppm)

- Hidrocarbonetos (resíduos do combustível)
- Resíduos carbonosos derivados da não combustão ou queima incompleta do combustível.
- É um gás muito tóxico.
- É resultante das partes fraccionadas das cadeias longas do combustível que não se oxidaram.
- Menor concentração de HC => melhor combustão

NO_x (%vol)

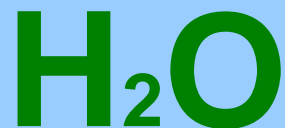
- Óxido de nitrogênio
- Formados pela mistura de oxigênio e nitrogênio
- Combinação do oxigênio com nitrogênio durante a combustão.
- A formação destes óxidos é favorecida pela alta **temperatura** do motor
- É um gás muito tóxico e contribui para a diminuição da camada de ozônio

CO₂ (%vol)

- **Dióxido de Carbono**
- **Resultante da combustão**
- **Pouco tóxico em baixas concentrações**
- **Maior concentração de CO₂ => melhor combustão**

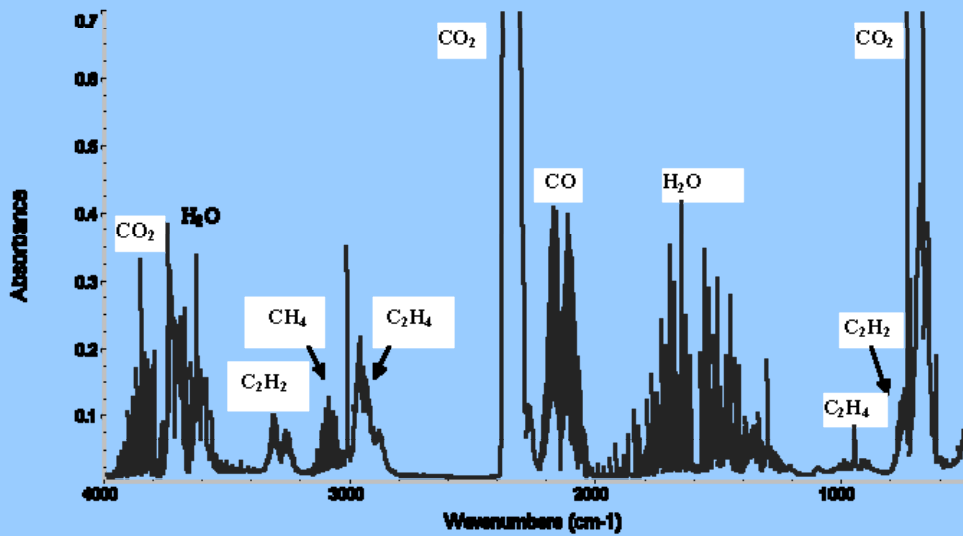


- Oxigénio
- Numa combustão ideal, todo O₂ que entra no motor deveria ser usado na combustão
- Menor concentração de O₂ => melhor a combustão

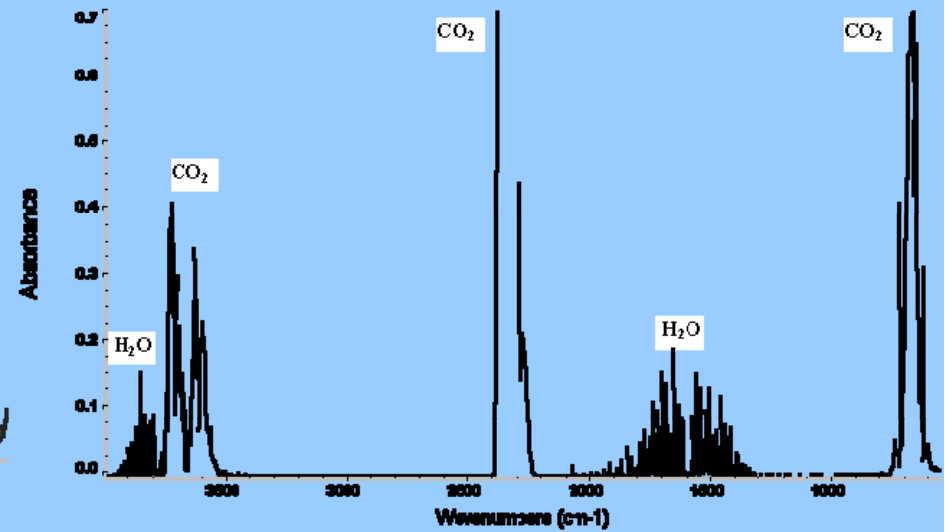


- Vapor de água
- Resultante da combustão

1942



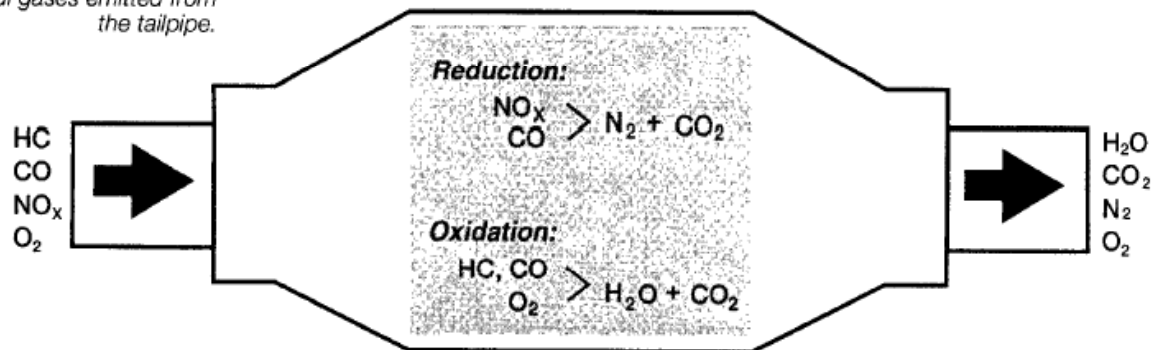
2002

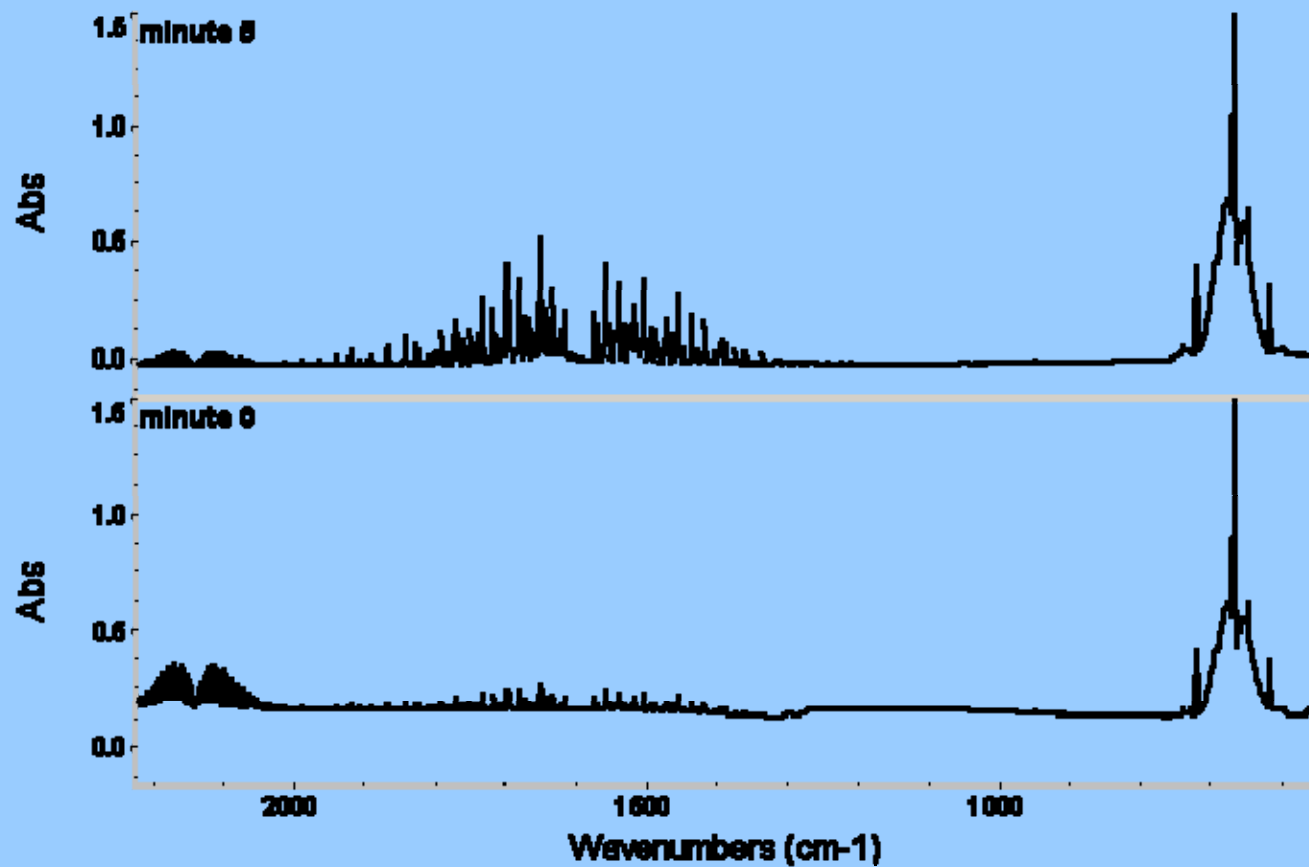
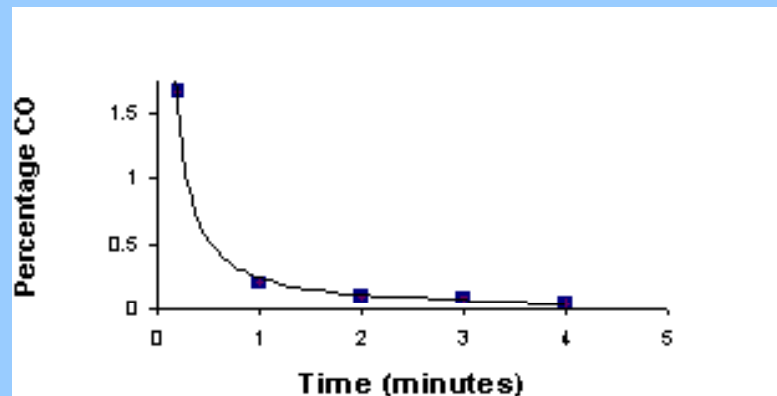


Secondary Combustion

Catalyst reduction and oxidation occurs in the TWC to further reduce the level of harmful gases emitted from the tailpipe.

Oxidation and Reduction Process



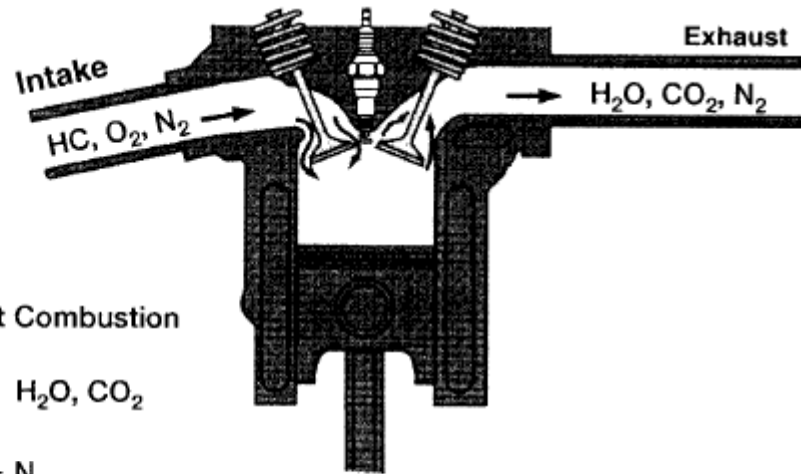


Ensaio

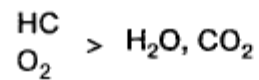


"Ideal" Combustion

If "perfect" combustion were to occur, hydrocarbons (HC) would be oxidized into water (H_2O) and carbon dioxide (CO_2). Also, nitrogen (N_2) would pass through unaffected.

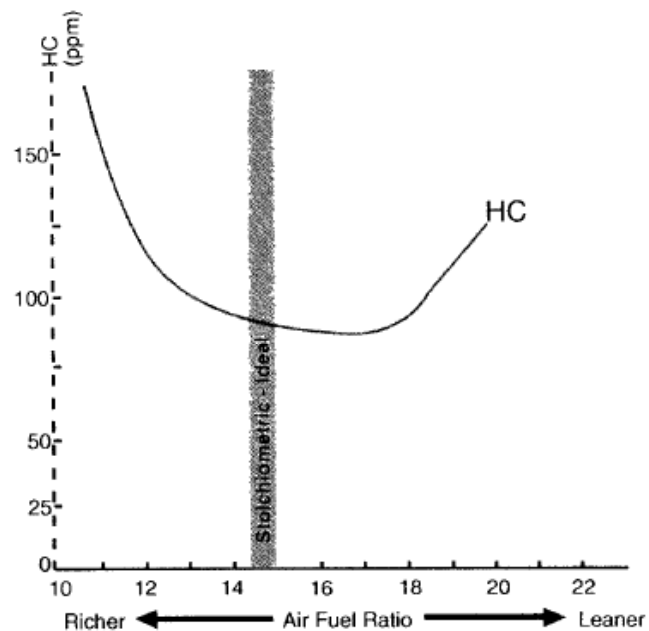


Perfect Combustion



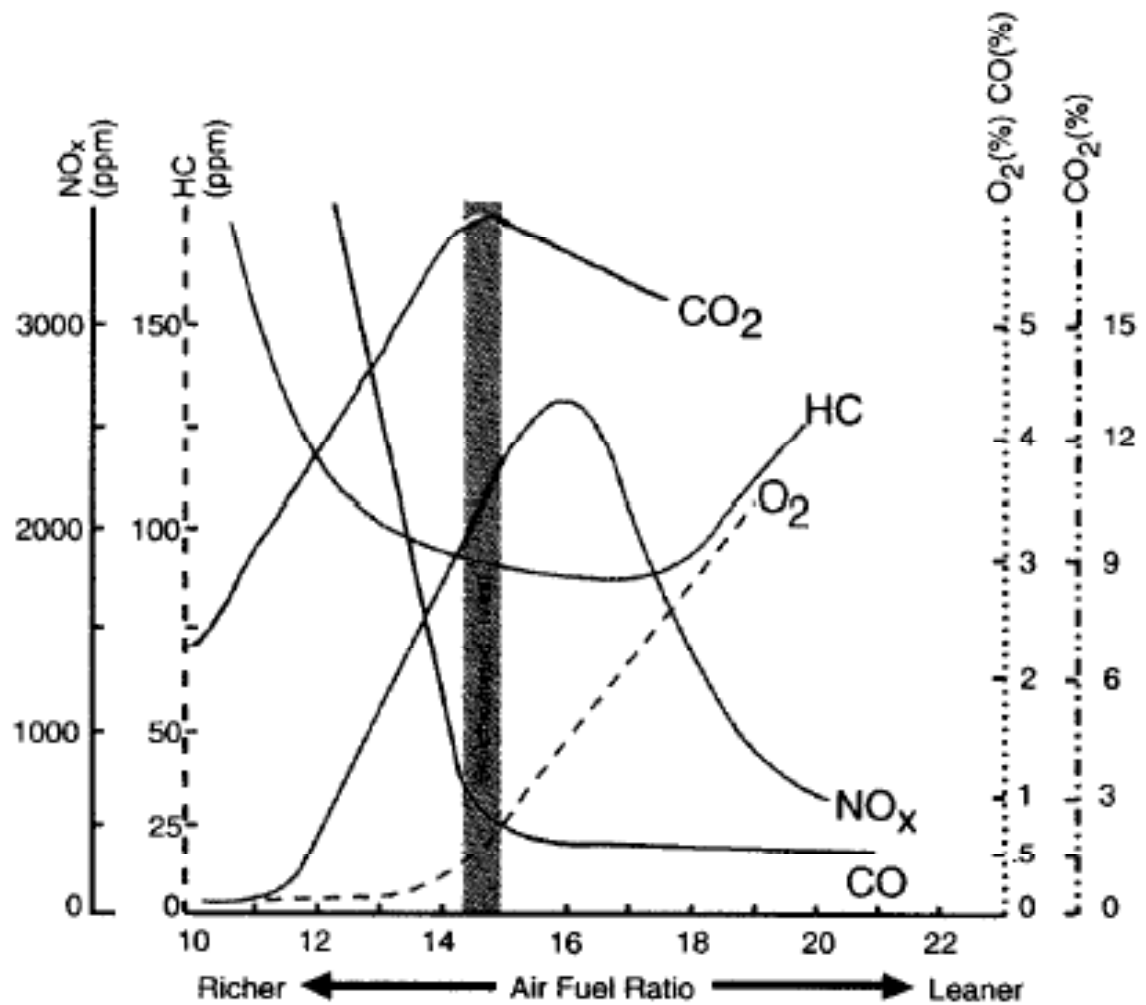
Effects of A/F Ratio on Exhaust HC

As shown, exhaust HC production is lowest when A/F ratio is slightly leaner than "ideal"; however, HC's increase dramatically when the mixture becomes too rich or too lean to the point of misfire.

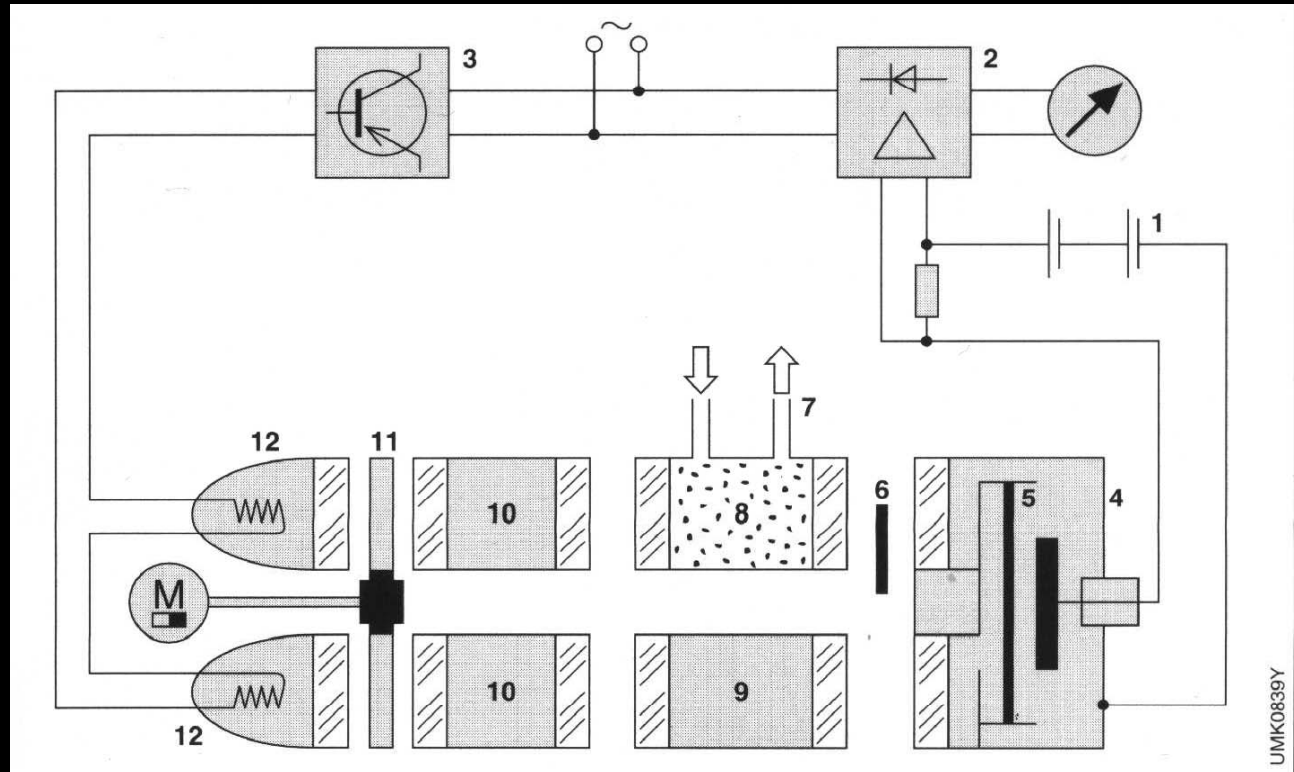


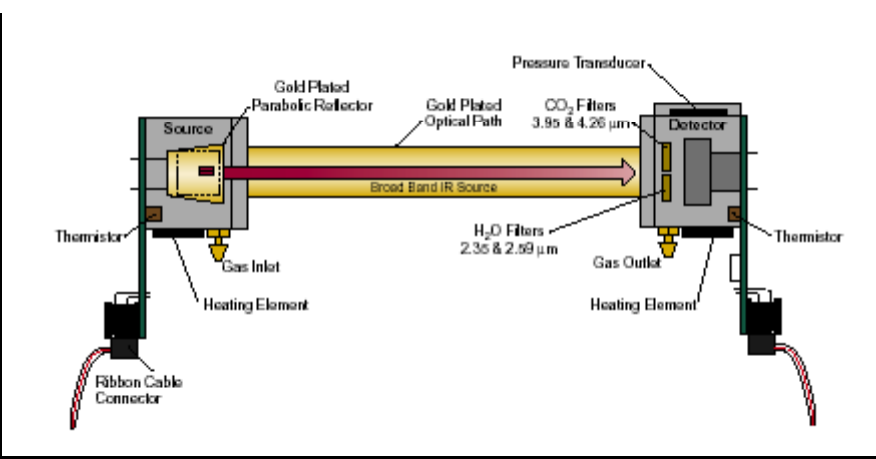
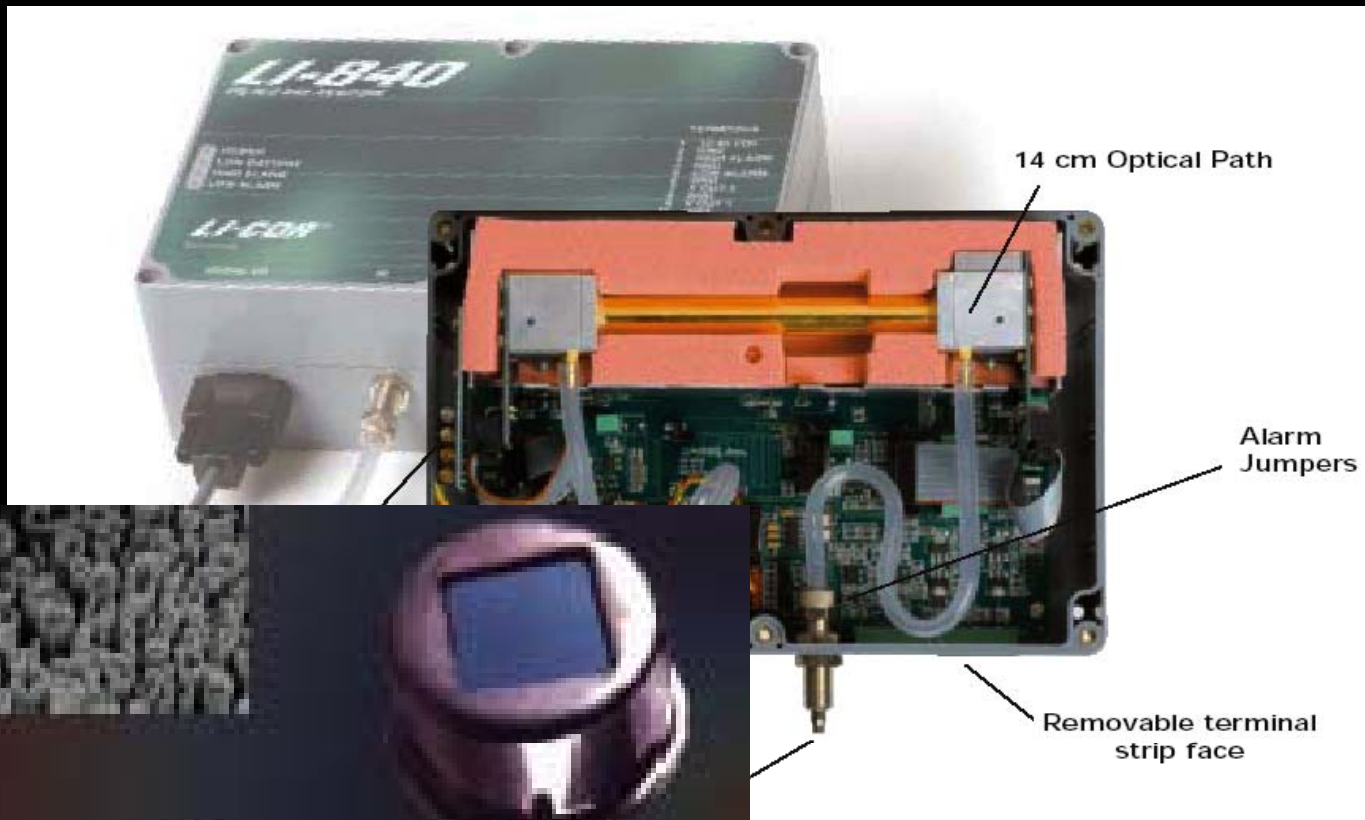
Effects of A/F Ratio on Exhaust O₂

Exhaust O₂ is lowest when A/F ratio is richer than "ideal"; however, O₂ increases dramatically with leaner mixtures.

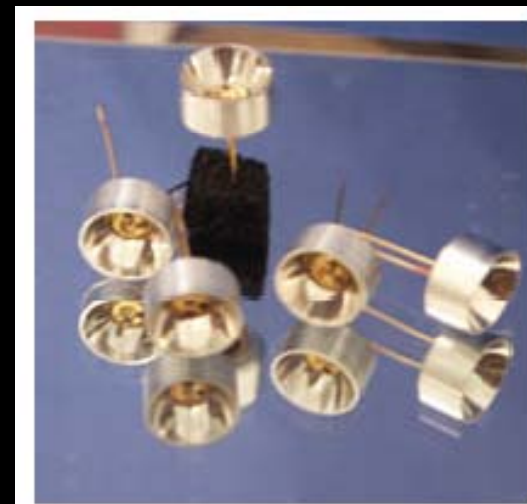
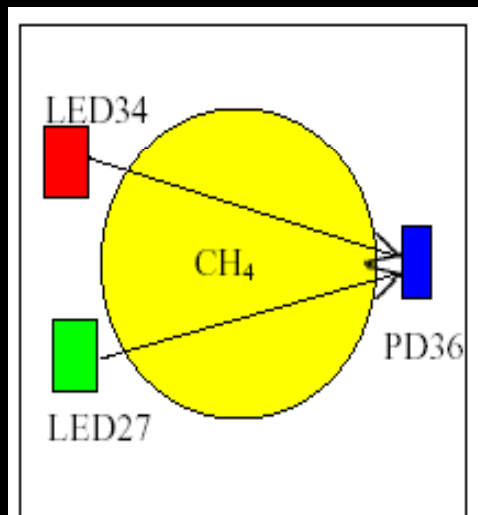
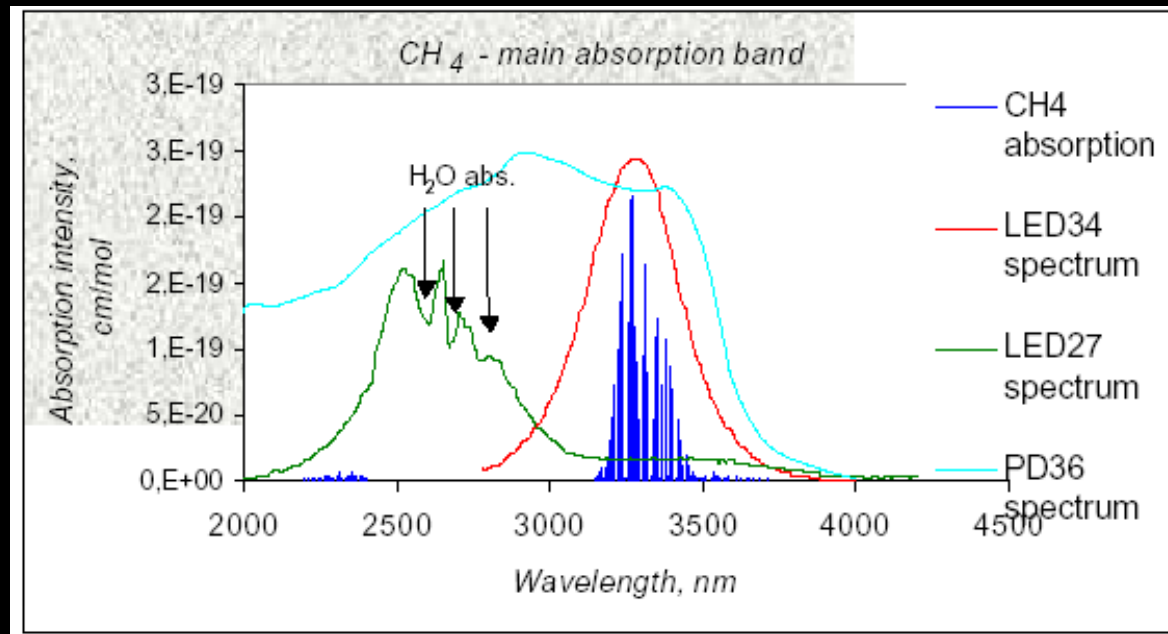


NDIR - Non-Dispersive Infra-red Detector - CO e CO₂





Sensor de Metano/Granja

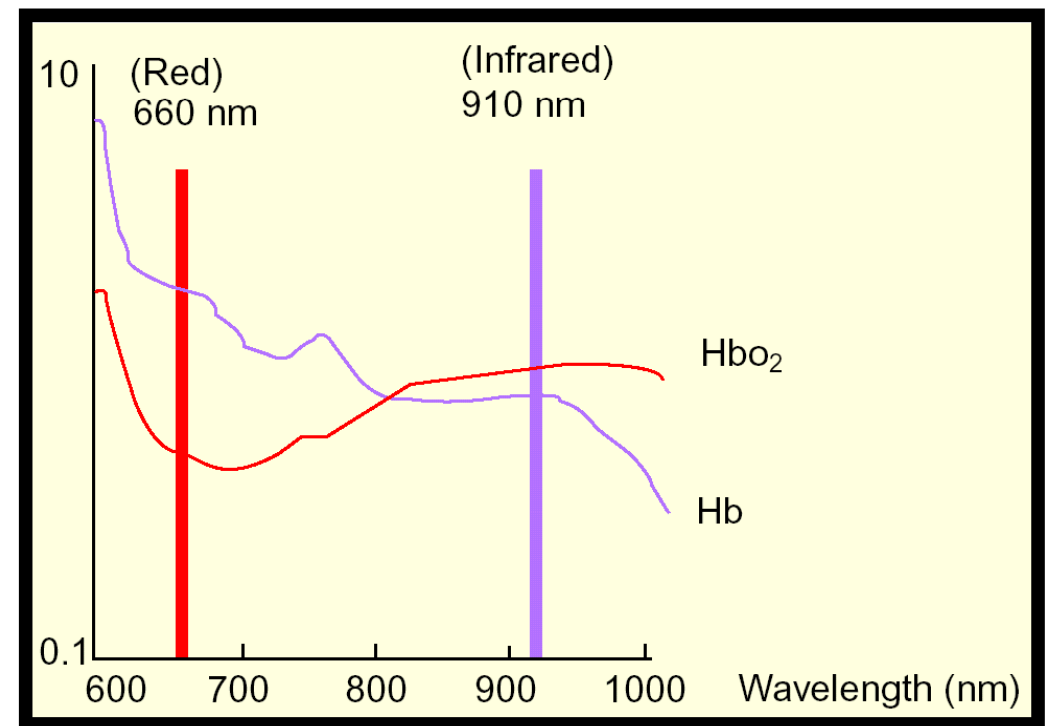
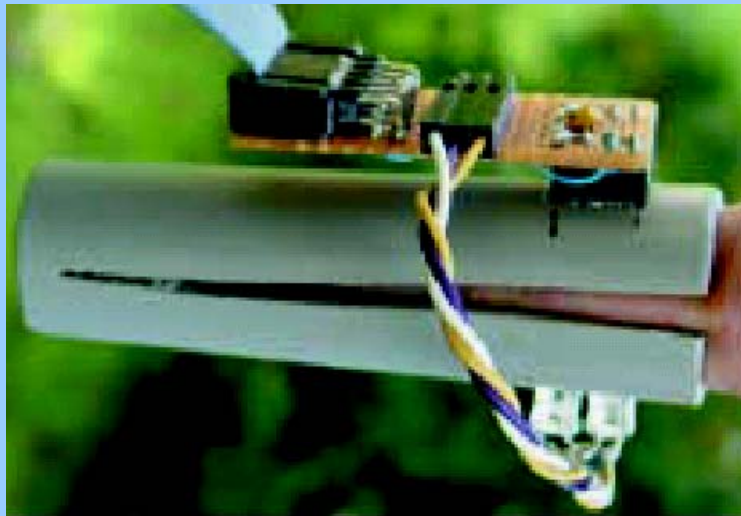




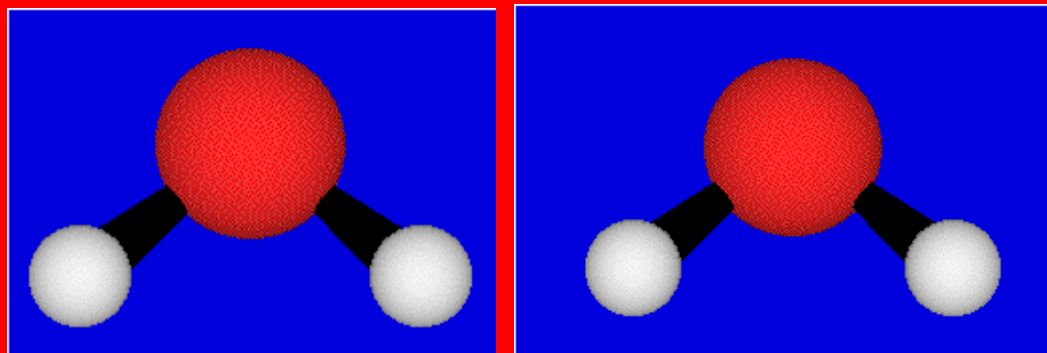
Oximetria Óptica

A oximetria óptica surgiu da observação de que o sangue oxigenado apresenta coloração vermelha e quando desoxigenado apresenta coloração Azulada.

Saturação de Oxigênio
Wood (1949)



Níveis de Energia
Impressão Digital
de um
Sistema Atômico



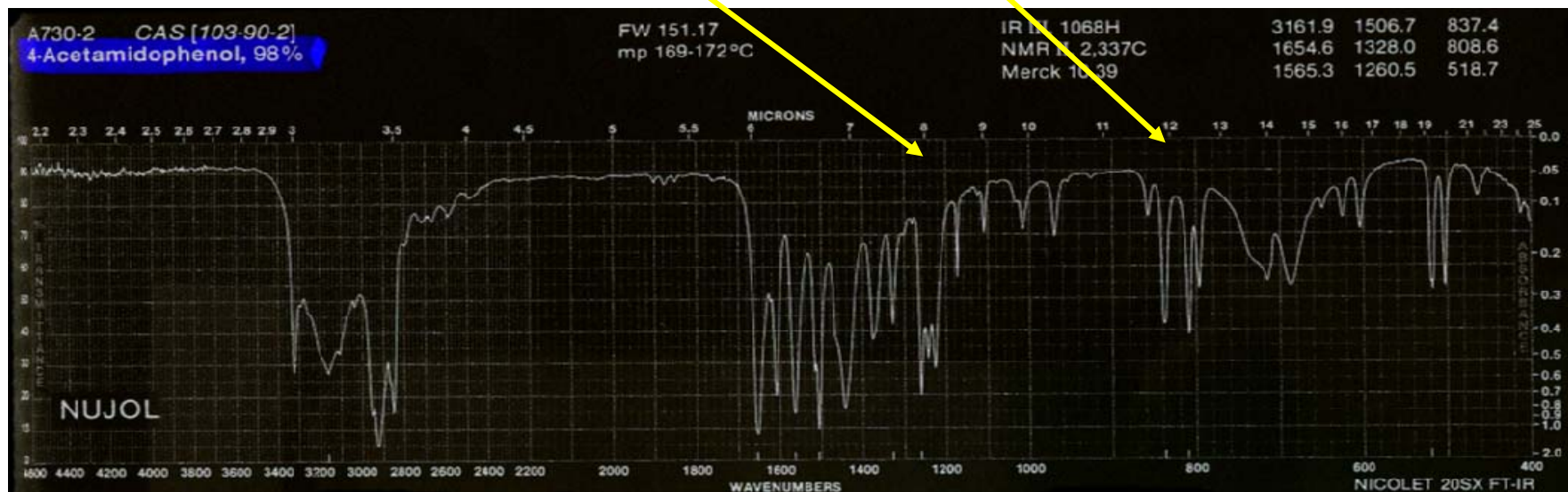
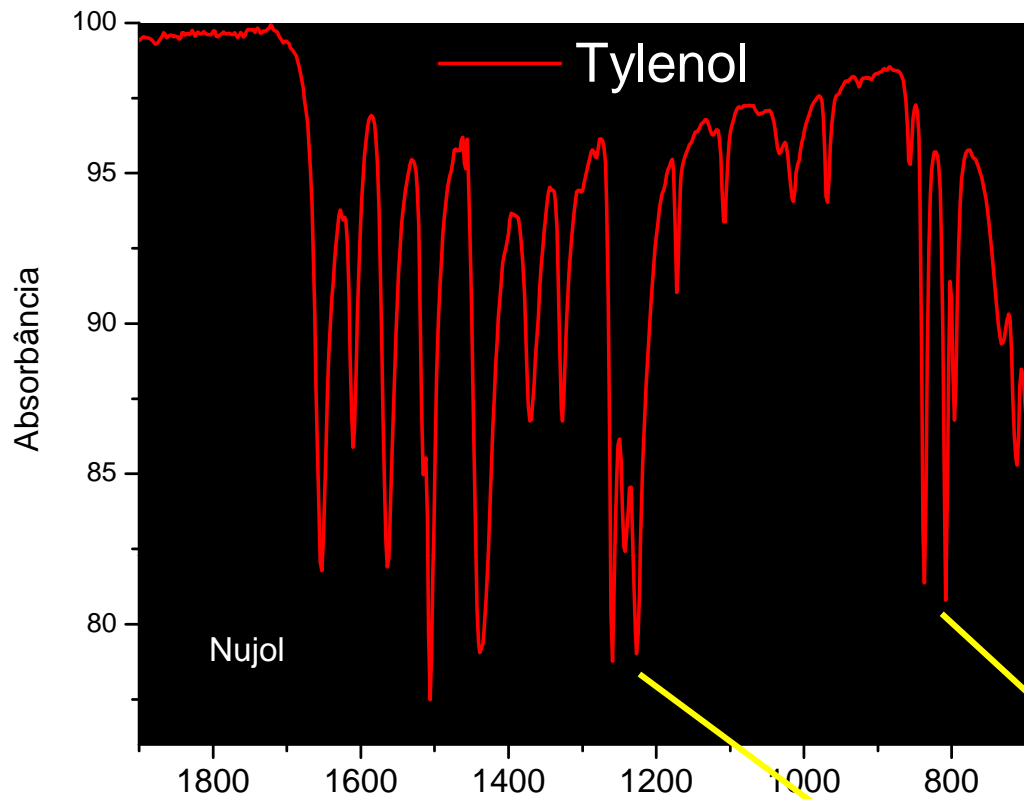
Comprimento de Onda (μm)

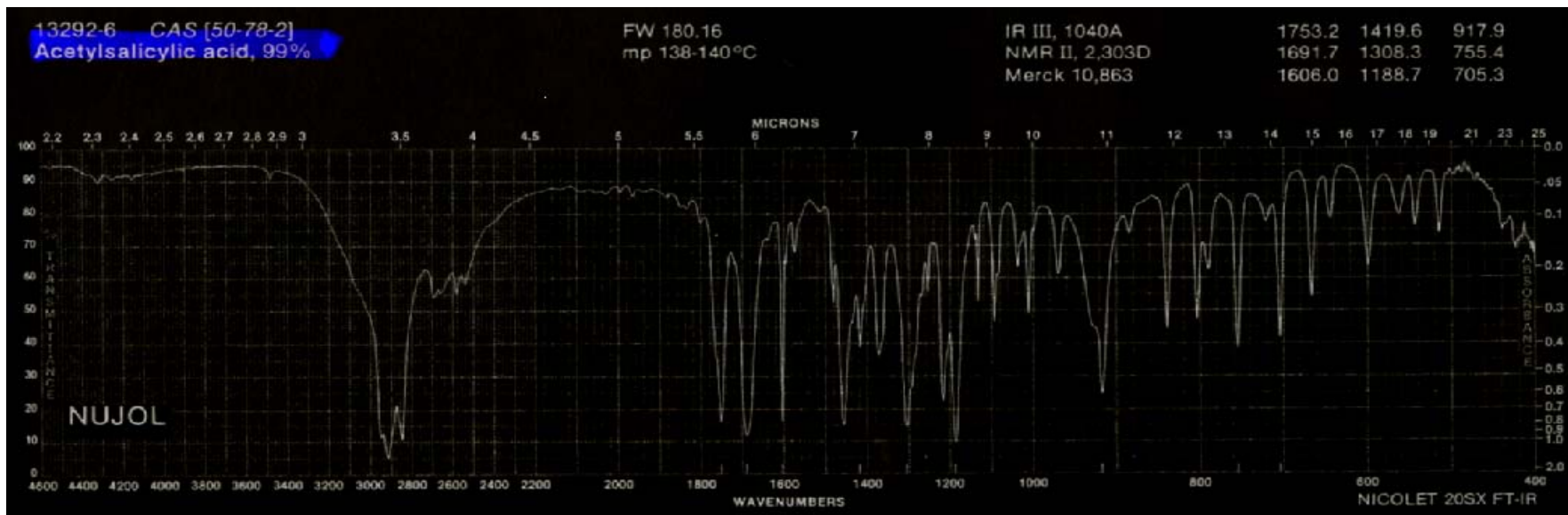
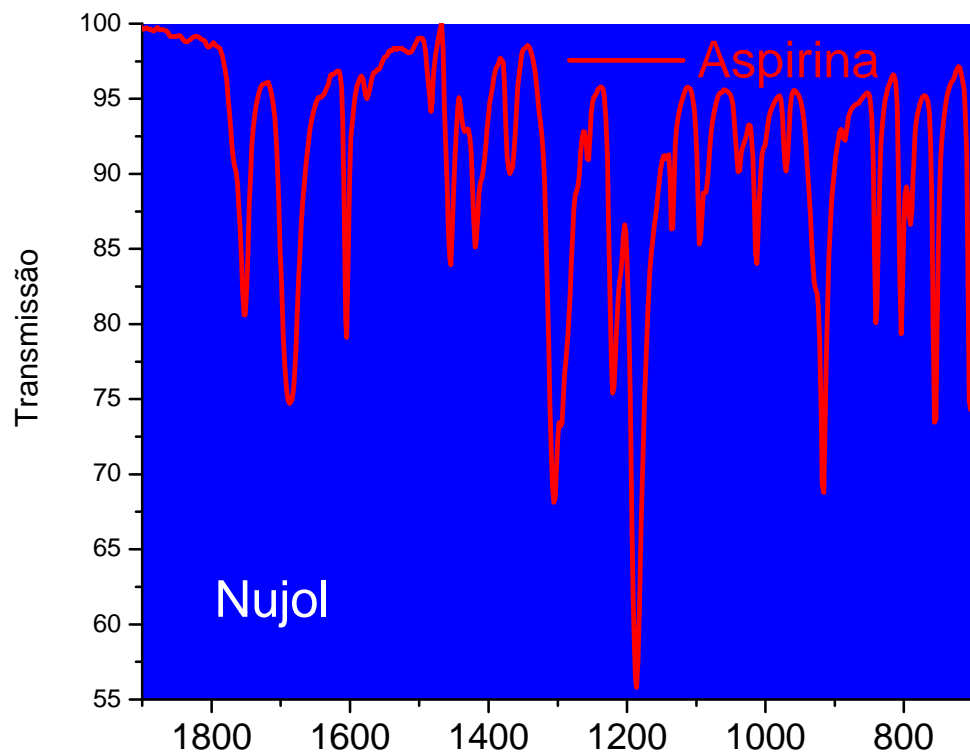
2.5 4.0 5.0 5.5 6.1 6.5 15.4

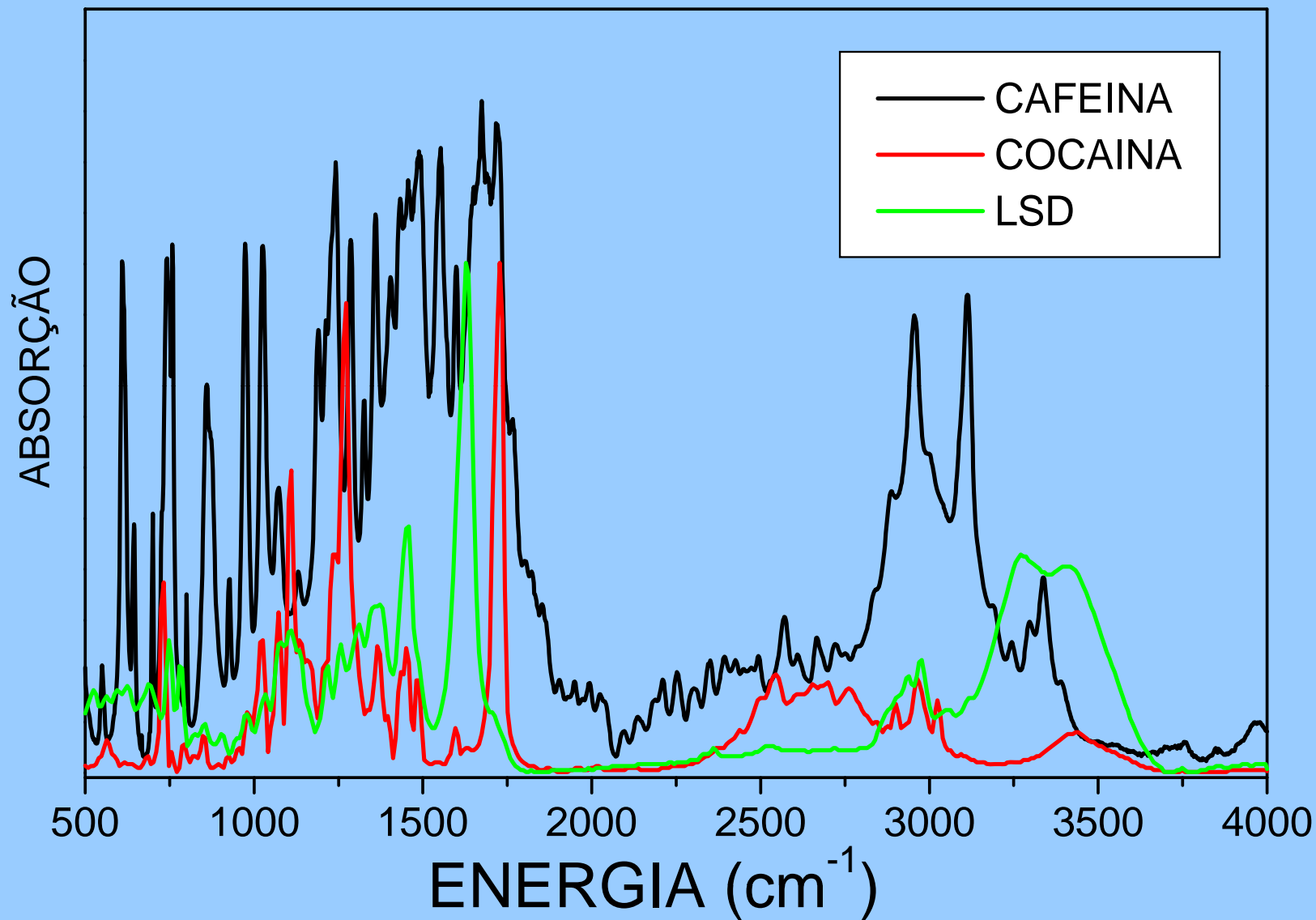
O-H	C-H	C \equiv C		C=O	C=N	C-Cl
N-H		C \equiv N				C-O
		X=C=Y (C,O,N,S)			C=C	C-N
						C-C
						N=O

4000 2500 2000 1800 1650 1500 650

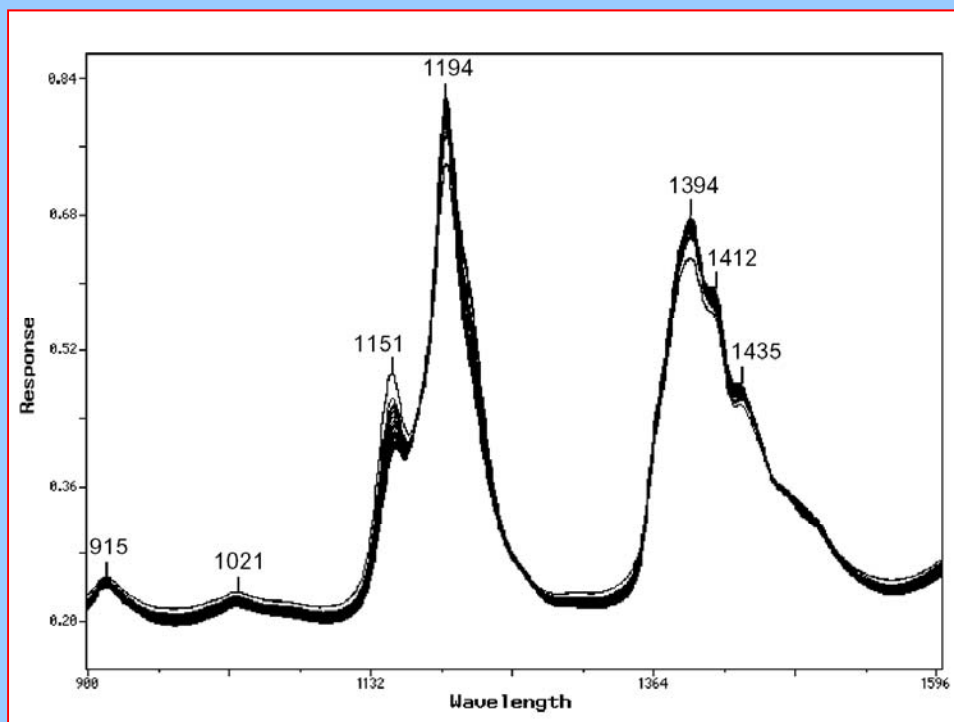
Frequência (cm^{-1})





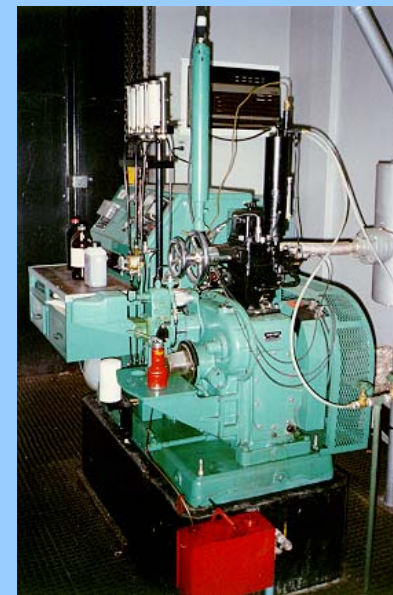


Determinação da Qualidade de Combustível

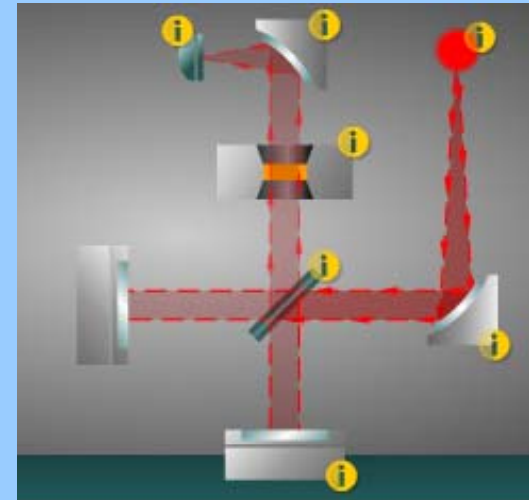
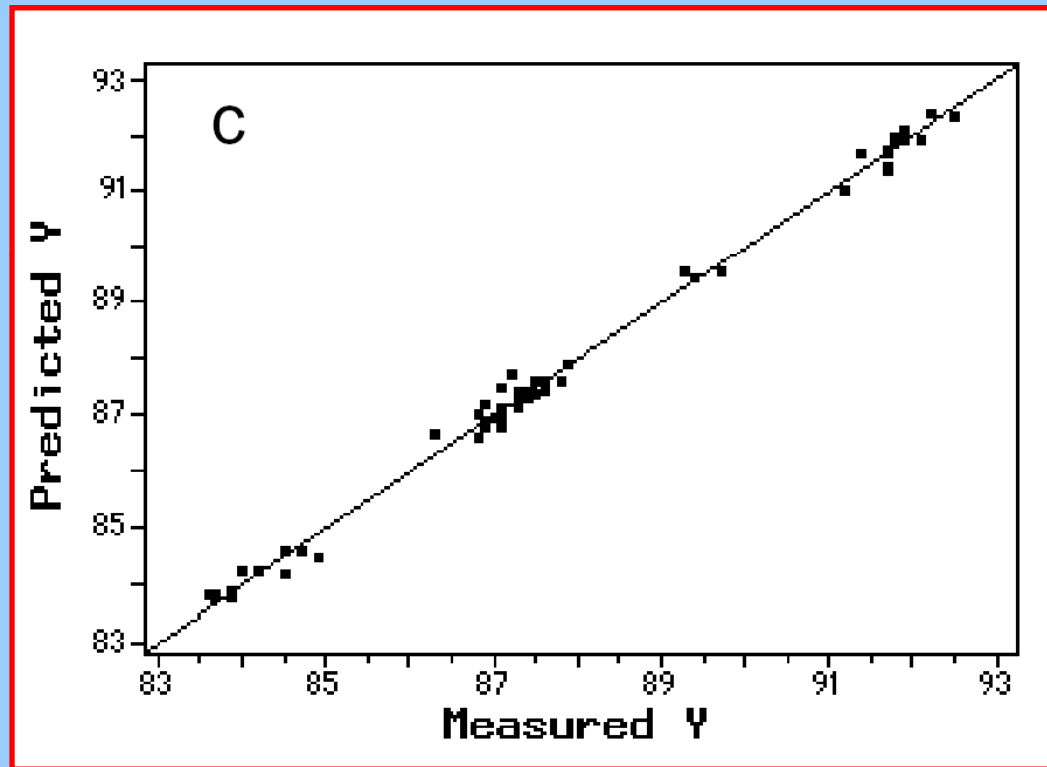


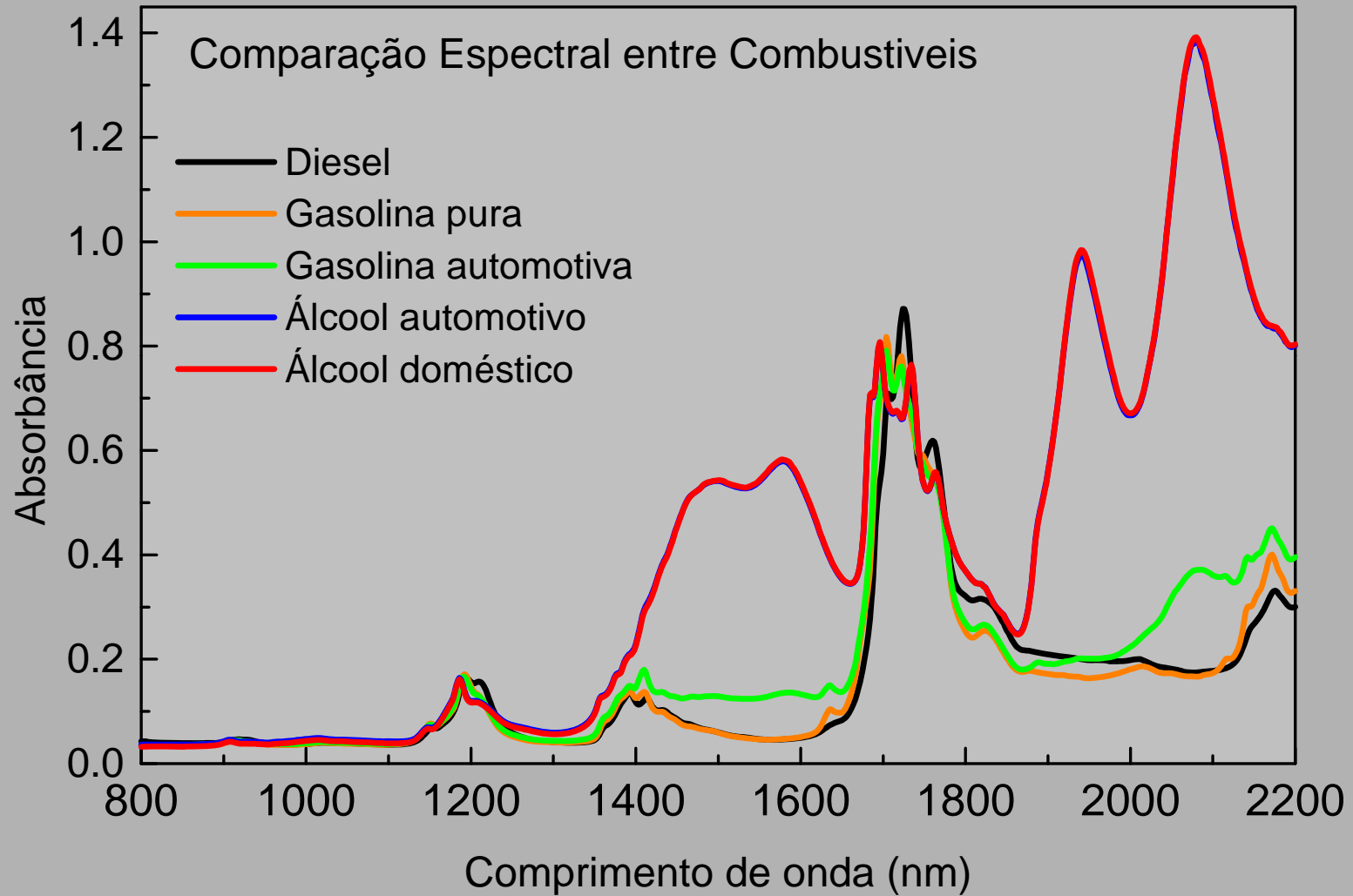
Wavelength	Assignment
915 nm	Stretch for CH ₂ (third overtone)
1021 nm	Combination bands for CH ₂ and CH ₃
1151 nm	Stretch for aromatic and CH ₃ (second overtone)
1194 nm	Stretch for CH ₃ (second overtone)
1394 nm	Combination bands for CH ₂
1412 nm	Combination bands for aromatic and CH ₂
1435 nm	Combination bands for aromatic and CH

Testes Químicos

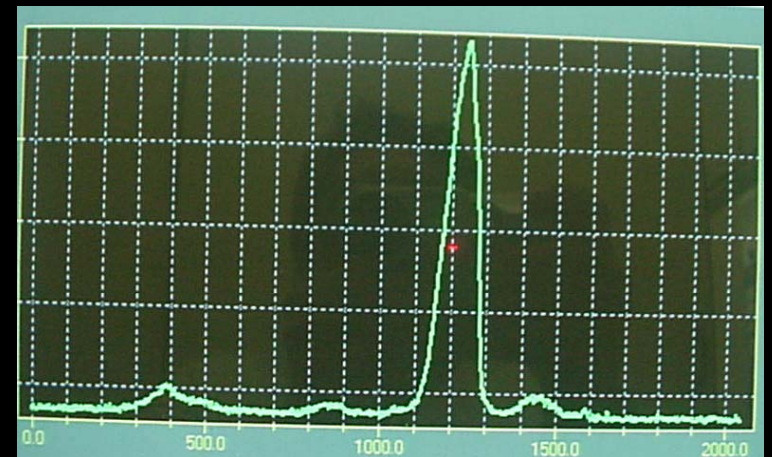


PLS-Partial Least Squares Regression





Marcador para Cédula



Detecção de Óleo em Água



Journal of Hazardous Materials 102 (2003) 39–55

**Journal of
Hazardous
Materials**

www.elsevier.com/locate/jhazmat

A literature review of portable fluorescence-based oil-in-water monitors

P. Lambert

Emergencies Science and Technology Division, Environment Canada, Ottawa, Ont., Canada K1A 0H3

350

400

450

500

550

600

650

λ [nm]

100ppm

Imunologia (Fluoroimunoensaio)

Marcadores são substâncias que emitem um sinal físico de intensidade proporcional a sua quantidade.

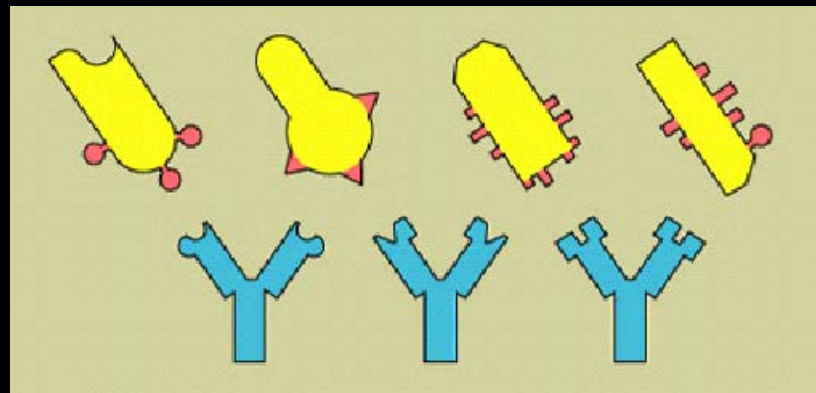
Radioisótopos

Enzimas

Fluorescentes

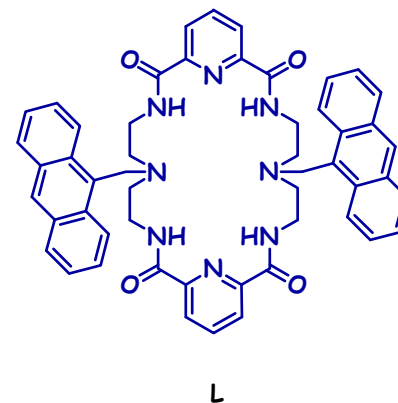
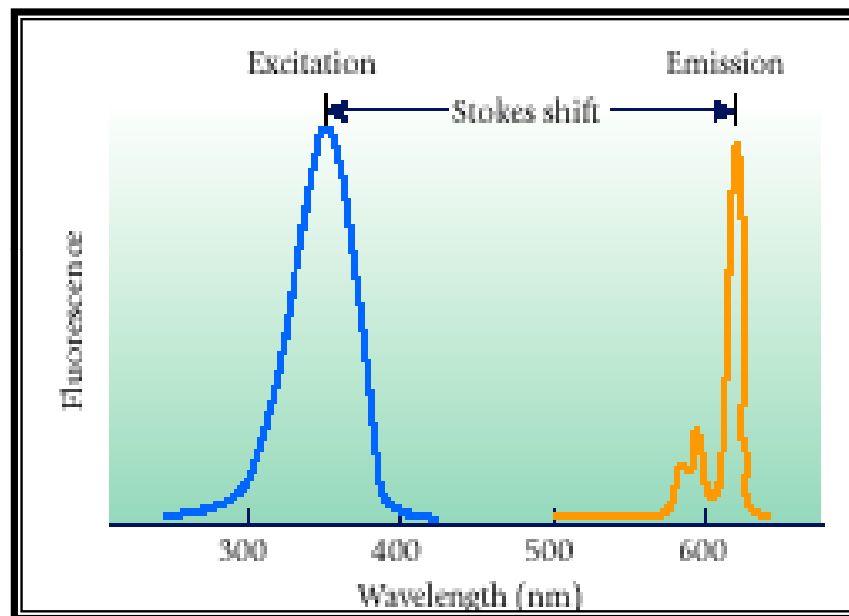
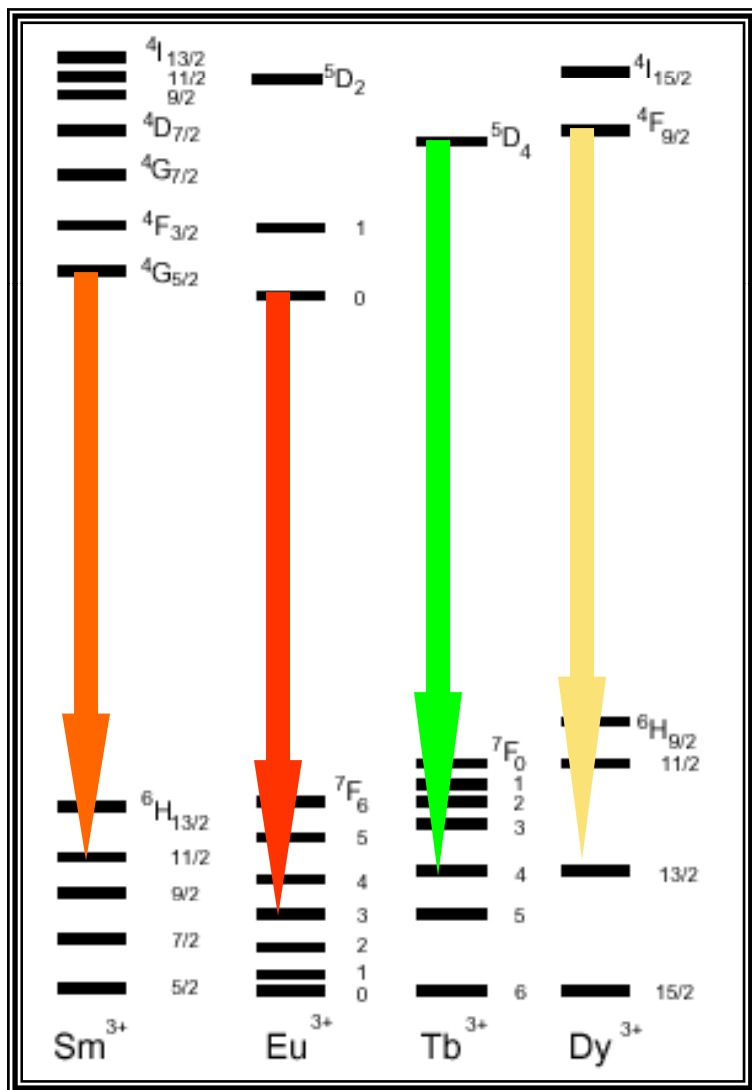
ANTÍGENO

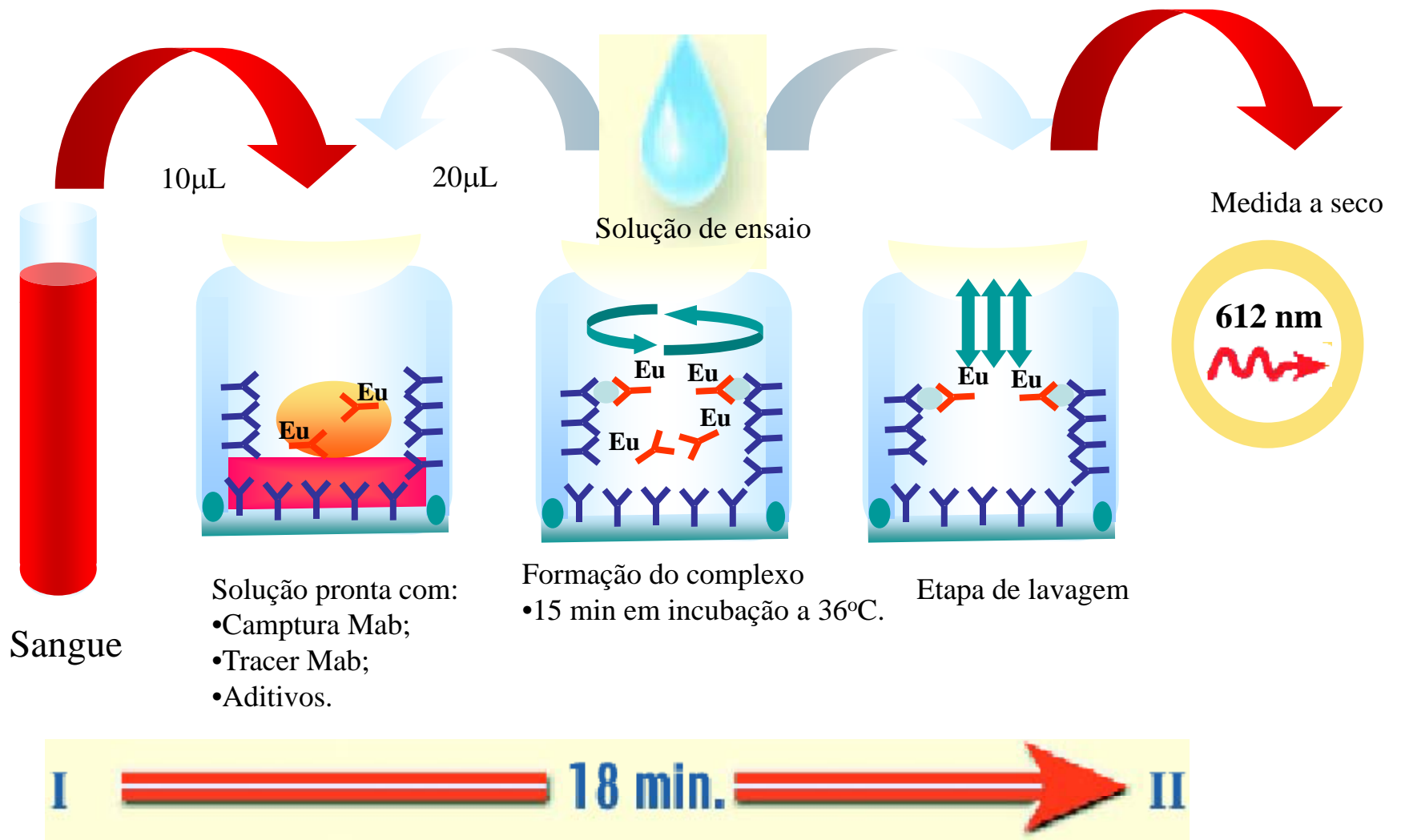
Nome dado às substâncias que, penetrando no organismo, são capazes de provocar a formação de substâncias protetoras chamadas anticorpo.



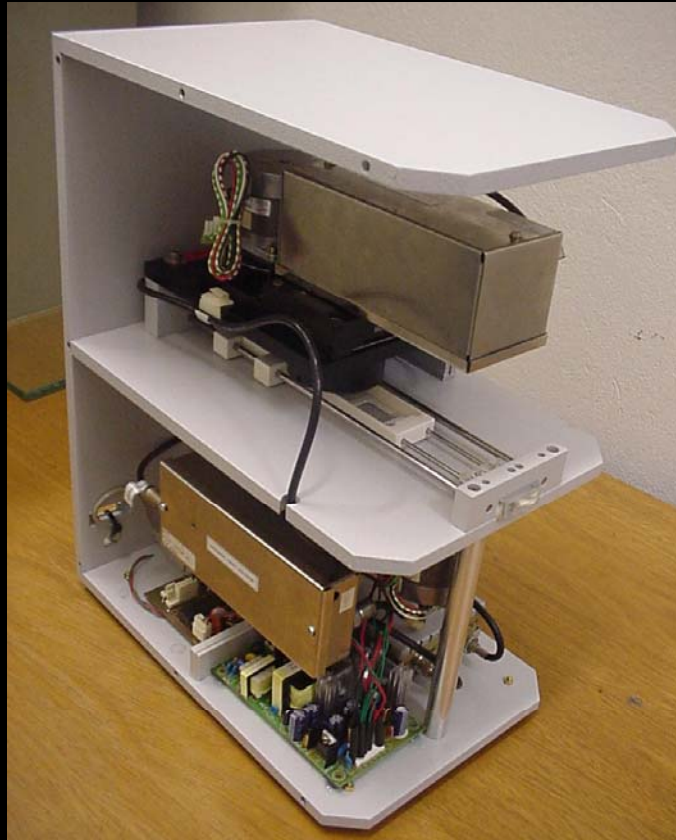
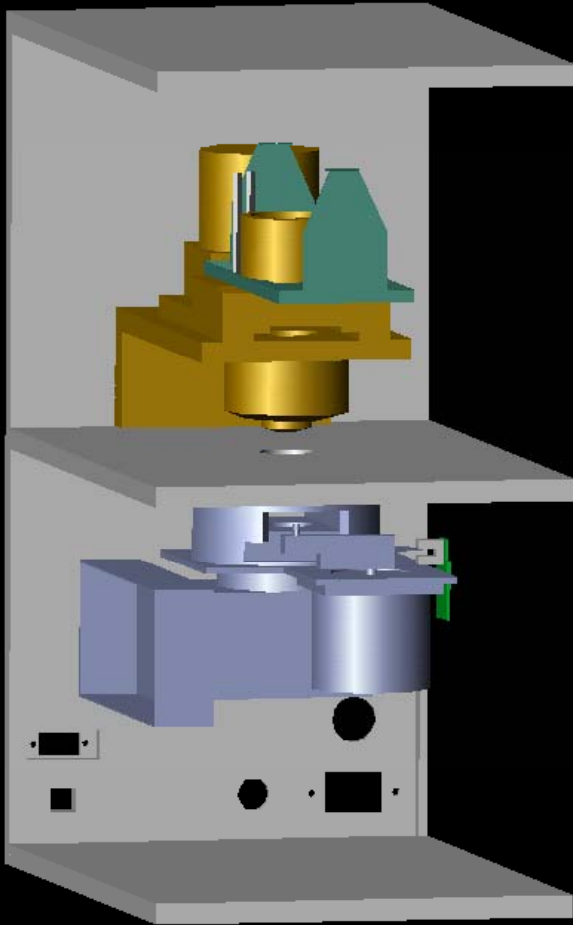
Marcadores Luminescentes (complexos de Ln^{3+})

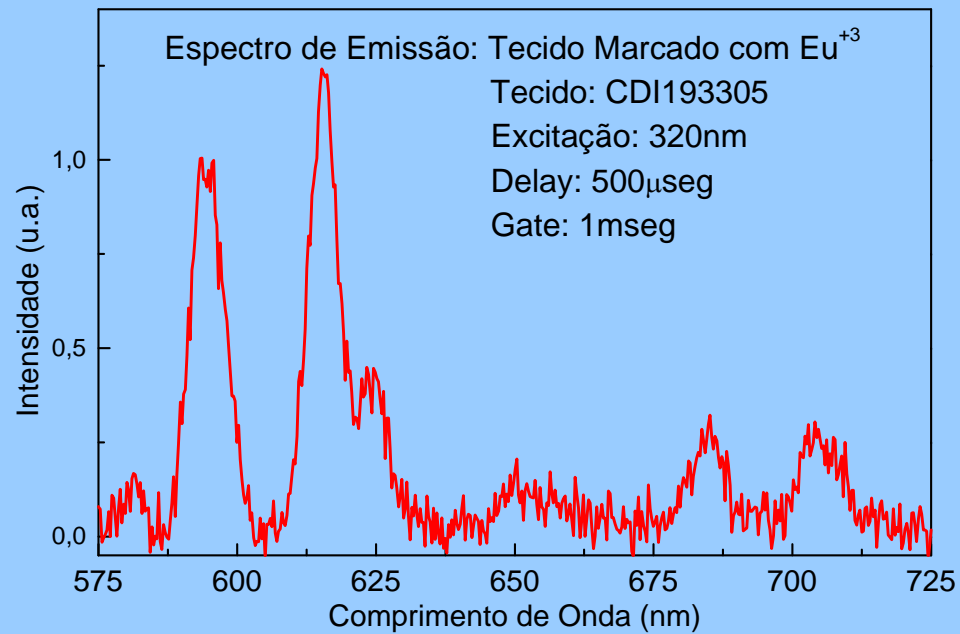
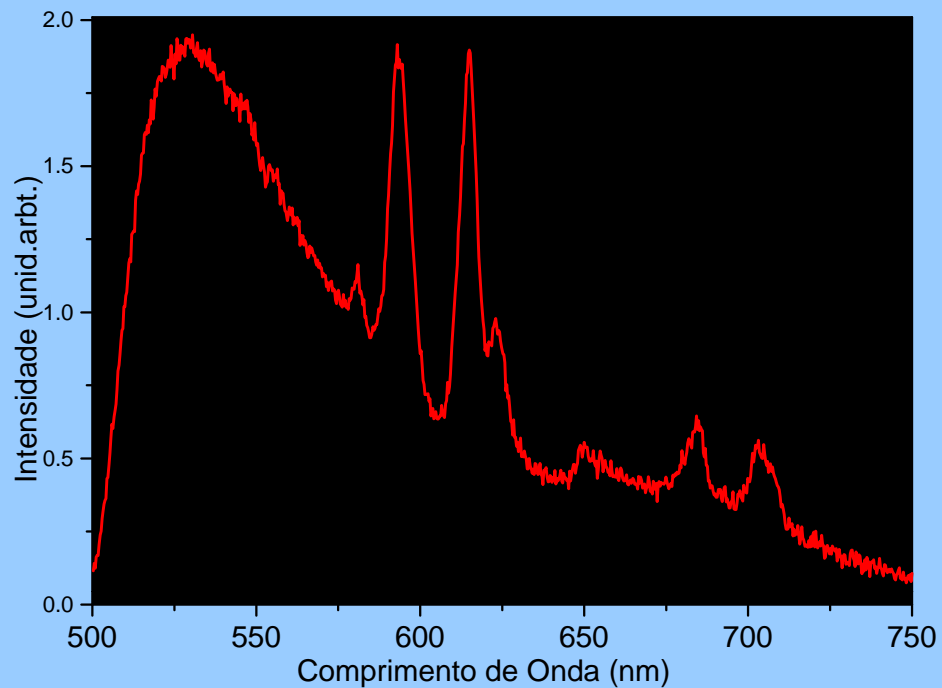
La Ce Nd Pm **Sm** **Eu** Gd **Tb** **Dy** Ho Er Tm Lu





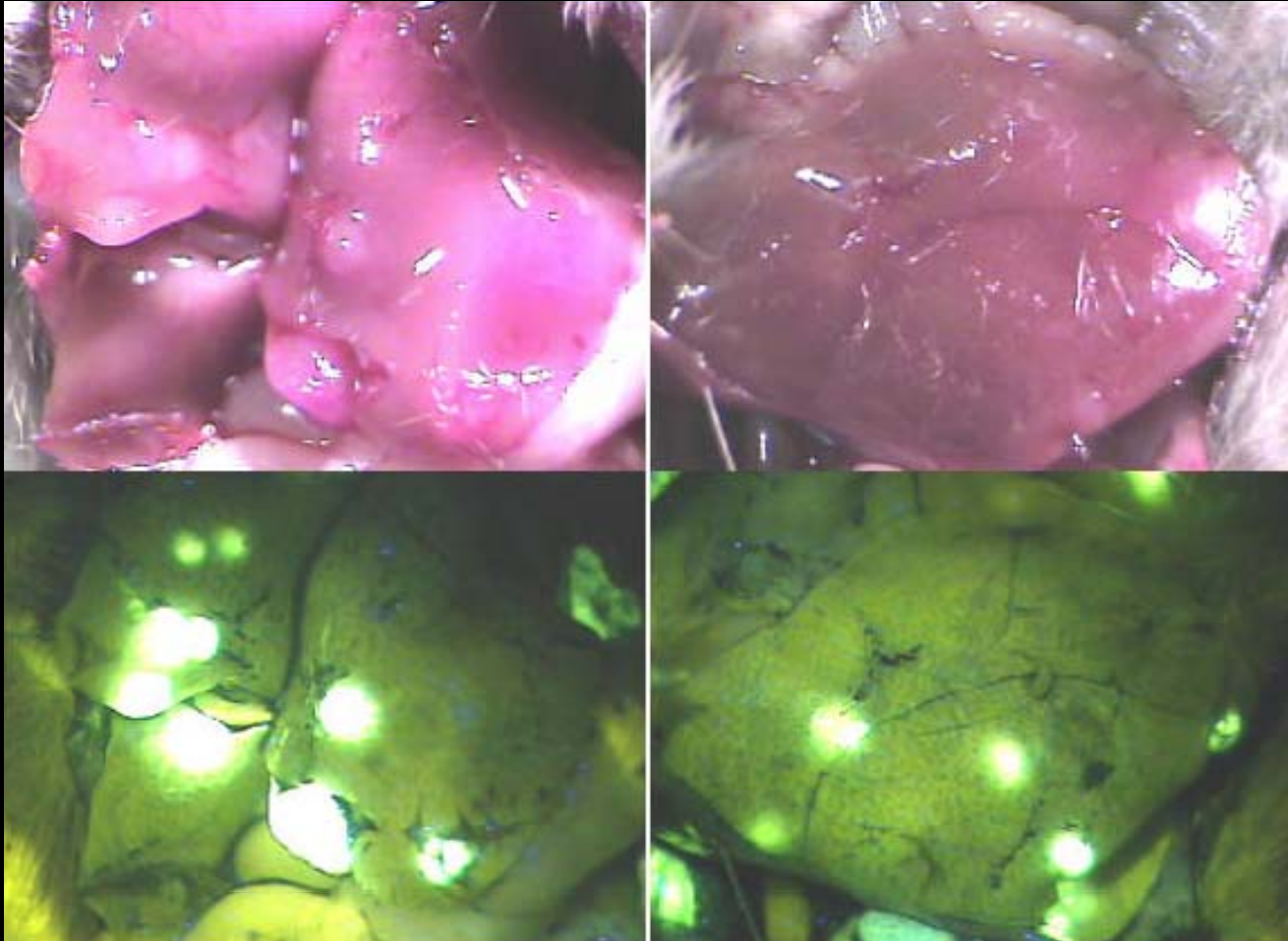
Projeto *Fluorim 1.0* - RENAMI





*Terras Raras:
Aplicações Industriais e Tecnológicas
Química Nova Vol.28, 111-117 - 2005*

Fluoreceina/Rodamina



Aplicações Criminalística



Fluoresceína + Hemoglobina



A horizontal rainbow gradient background, transitioning from red on the left to purple on the right, with yellow, green, and blue in between.

FIM