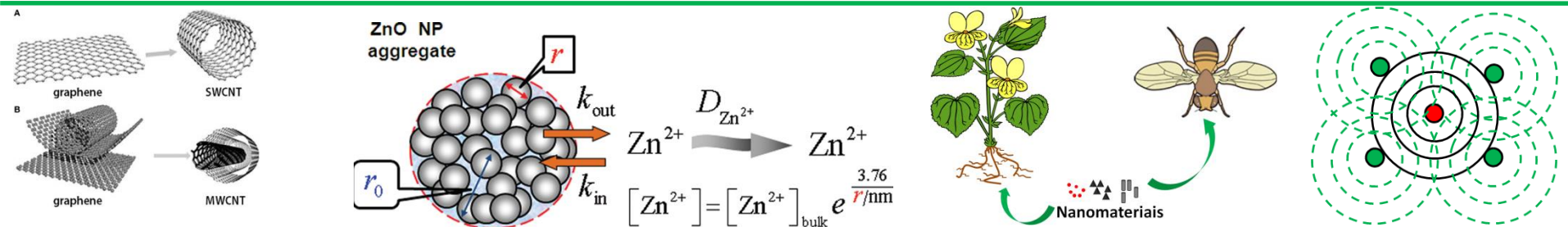




Introduction to X-ray Fluorescence Spectroscopy

Prof. Hudson W.P. Carvalho

Grupo de Espectroscopia Aplicada ao Estudo de Nanomateriais na Agricultura e no Ambiente
Laboratório de Instrumentação Nuclear



Main Features of XRF

- ❑ Qualitative analysis (from Na)

- ❑ Quantitative analysis

($\mu\text{g g}^{-1}$ EDXRF and ng g^{-1} TXRF)

- ❑ From Na to U (usually)

- ❑ Non-Destructive

- ❑ Minimum sample preparation is required

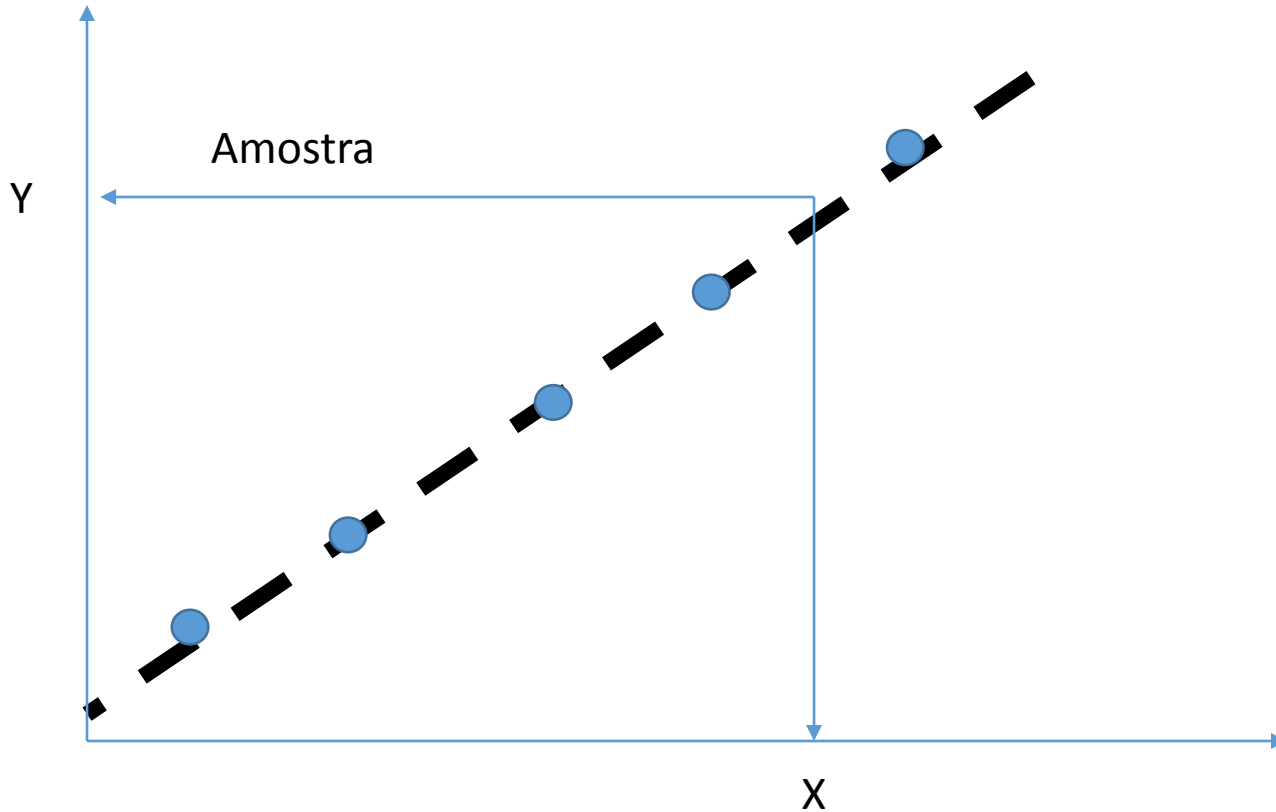
- ❑ **It may also give structural information**

Estratégias de Quantificação

Matrizes semelhantes

Taxa de contagens do elemento Fe

Exemplo: determinar a concentração de ferro em farinha de trigo



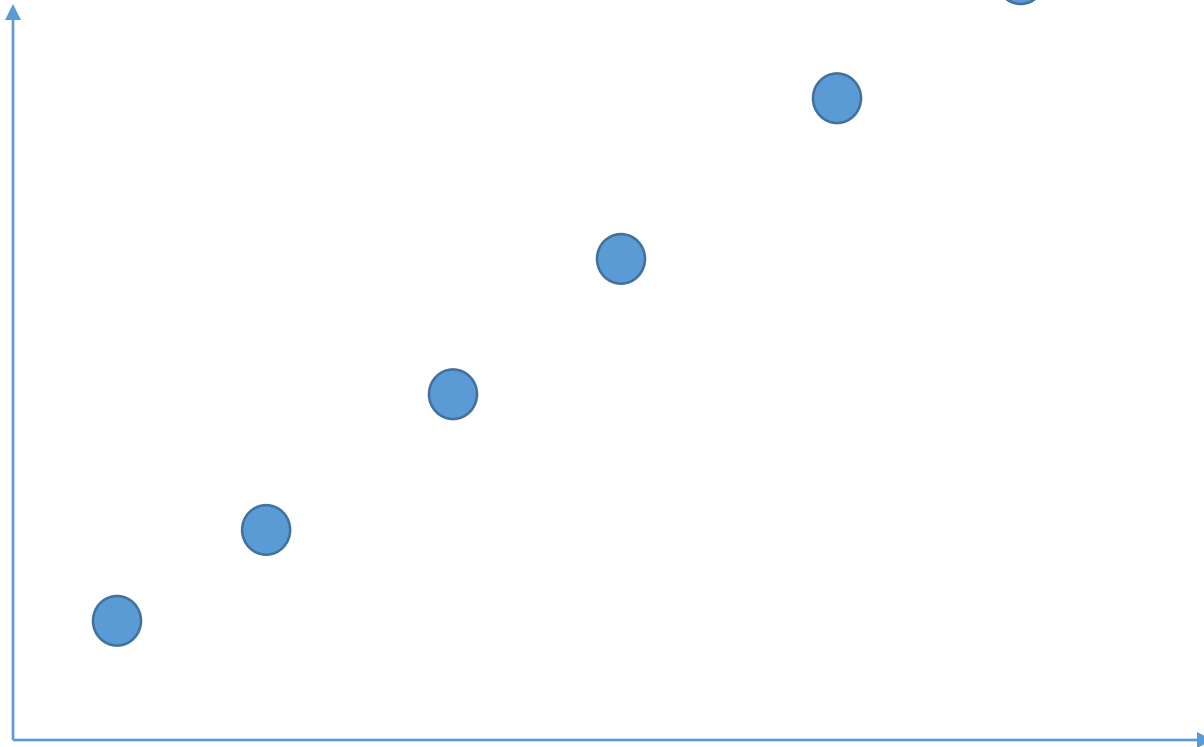
Matriz dos padrões:

Celulose, amido, compostos cujo número atômico médio sejam semelhantes àquele da amostra

Concentração de Fe nos padrões

Calibração cruzada

Taxa de contagens do elemento Fe



Método de Referência
(exemplo AAS ou ICP-OES)

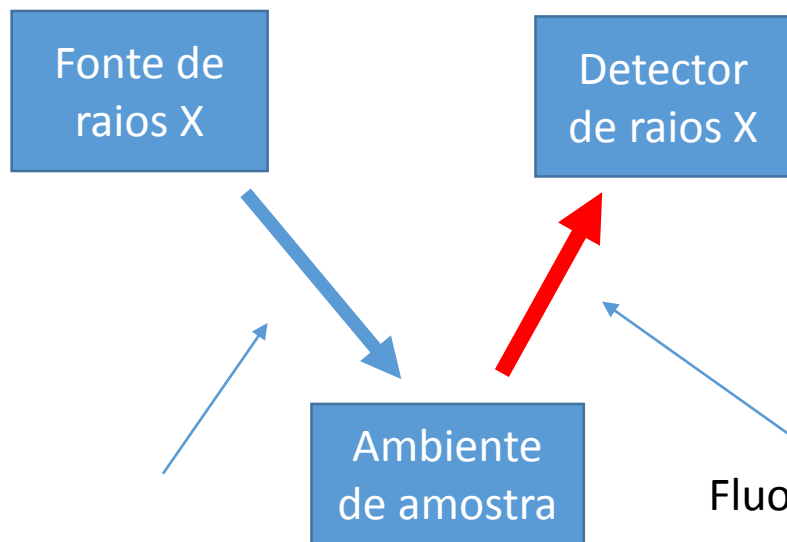
Trata-se de correlacionar a concentração
Encontrada por um método de referência com o sinal da XRF

Variantes da XRF

Os tipos de espectrômetros

□ Tipos de geometria

Detector capaz de contar fótons e identificar sua energia



EDXRF

Energy dispersive X-ray Fluorescence
Fluorescência de raios X por dispersão
de energia
ou dispersiva de energia

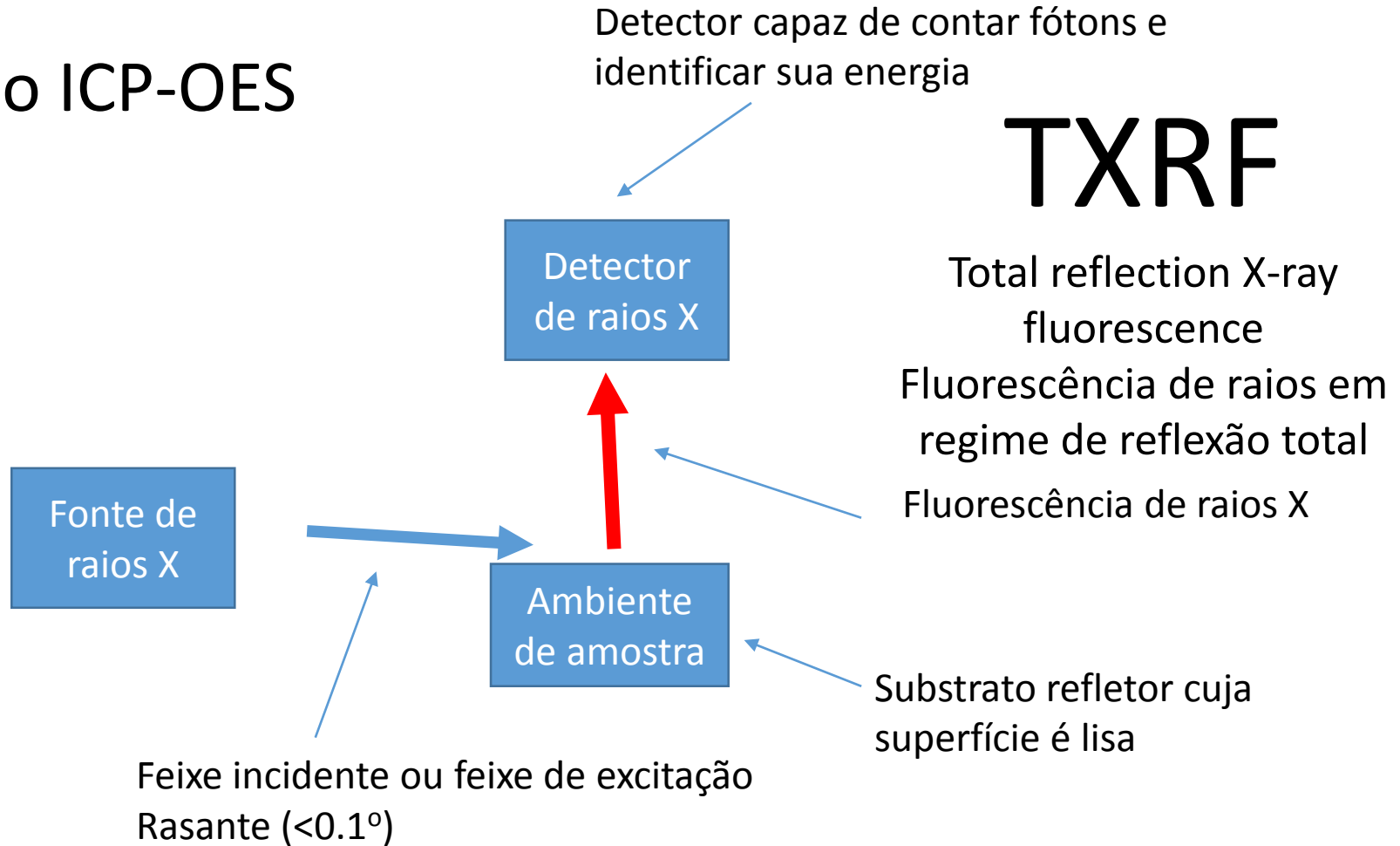
Fluorescência de raios X

Feixe incidente ou feixe de excitação

Os tipos de espectrômetros

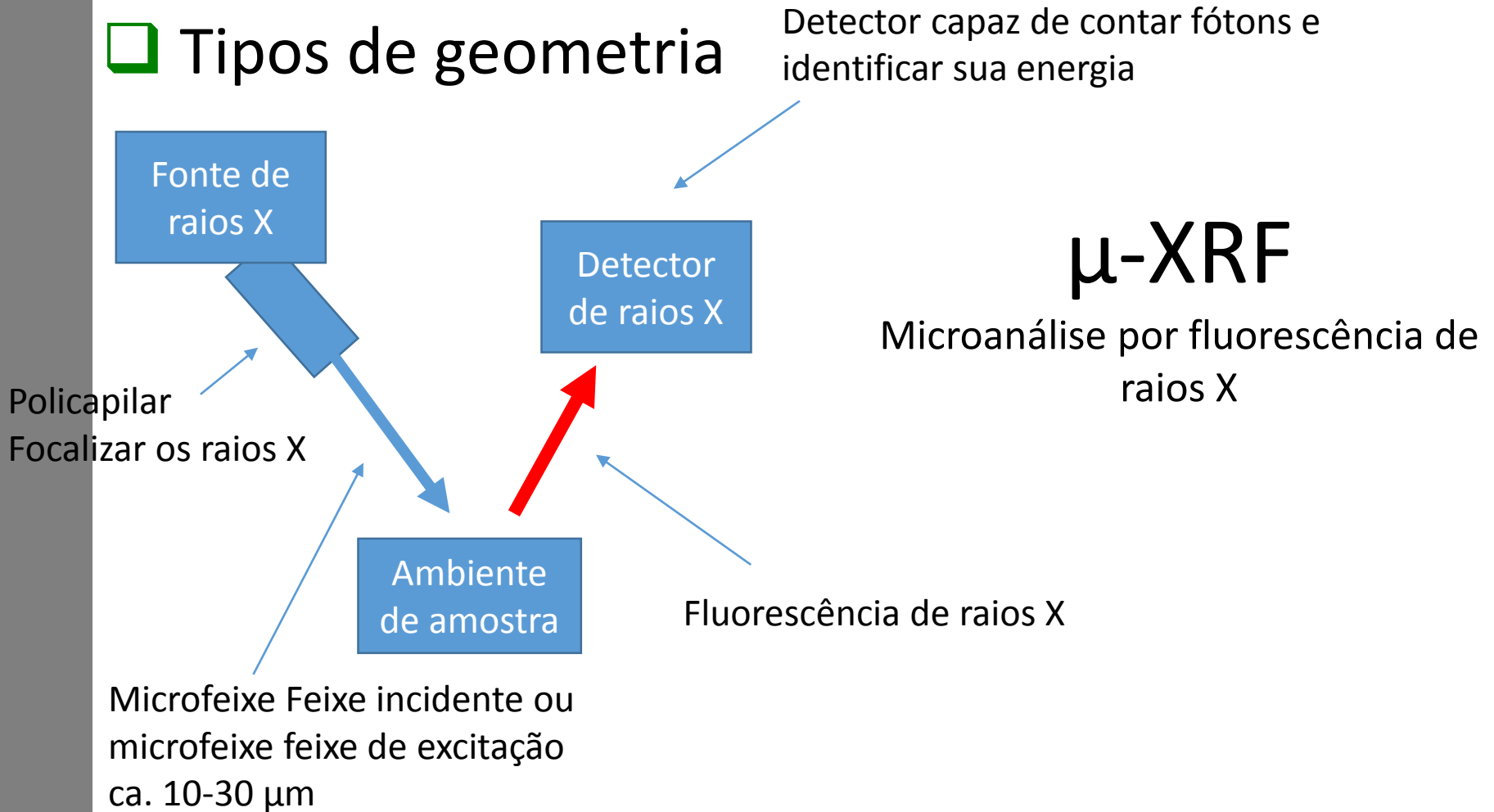
❑ Oferece limites de detecção comparáveis

ao ICP-OES



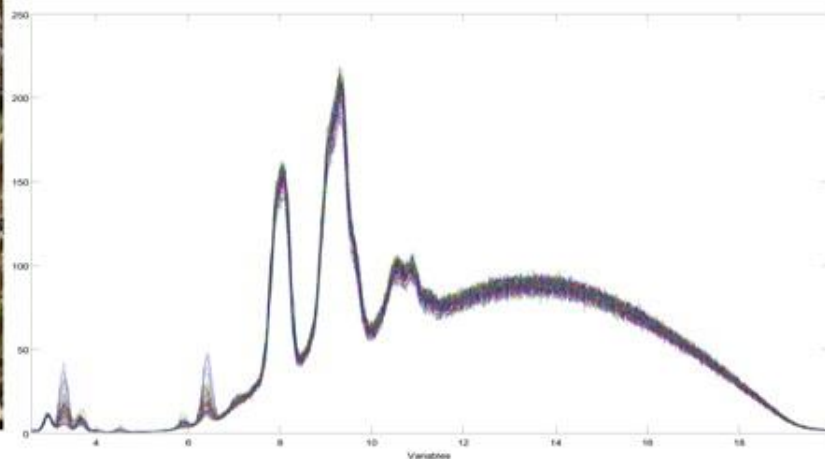
Os tipos de espectrômetros

□ Tipos de geometria

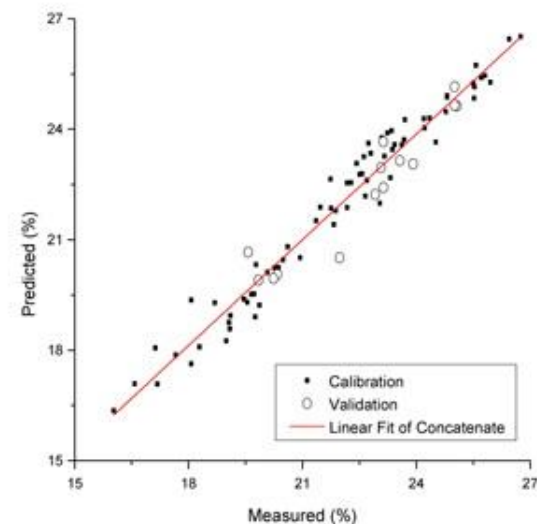


Aplicações de EDXRF

□ É possível determinar sacarose em cana



PLS Model for Sucrose



JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Article
pubs.acs.org/JA

Direct Determination of Sugar Cane Quality Parameters by X-ray Spectrometry and Multivariate Analysis

F. L. Melquiades,^{*,†,||} G. G. Bortoleto,[‡] L. F. S. Marchiori,[§] and M. I. M. S. Bueno^{||}

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[‡]Faculdade de Tecnologia de Piracicaba, Centro Paula Souza, Piracicaba, São Paulo, Brazil

[§]Estação Experimental, Fazenda Areão da Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, Piracicaba, São Paulo, Brazil

- ❑ Correlação entre o sinal de raios X e parâmetros de valoração
- ❑ É possível determinar a quantidade de açúcar e fibras na cana & proteína na soja

Eficiência

↑

economia de tempo e recursos

↑

Raios X



Screening of mineral elements in powdered milk by EDXRF



Sample



Pellet pressed



PANalytical

Element	Concentration range (mg/100g)	RMS* (mg/100g)	Correlation	LLD (mg/100g)
P	176 – 1020	23.2	0.9899	0.5
Cl	276 – 984	11.4	0.9971	0.2
K	416 – 1670	15.8	0.9978	0.6
Ca	278 – 1360	21.3	0.9959	0.3
Mn	0.0063 – 1.515	0.03	0.9981	0.05
Fe	4.90 – 9.16	0.26	0.9794	0.04
Cu	0.3 – 0.85	0.05	0.9411	0.06
Zn	3.66 – 7.69	0.15	0.9866	0.06

Table 2. Calibration details (* RMS: The more accurate calibrations have the smaller RMS values).

Element	Average concentration (mg/100g)	RMS (wt%)	Relative RMS (%)
P	234.8	2.1	0.9
Cl	292.3	2.9	0.9
K	442.3	2.2	0.5
Ca	368.3	2.1	0.6
Mn	0.06	0.02	28.7
Fe	5.42	0.10	2.6
Cu	0.40	0.04	9.3
Zn	3.75	0.06	1.7

Table 3. Results of the repeatability test of milk powder sample prepared as pressed pellet

in milk powder

RoHS- Restriction of Certain Hazardous Substances



PVC discs



Element	Limit (mg/kg)
Pb, Hg, Cr ⁶⁺ , Br in PBBs and PBDEs	1000 (~300)*
Cd	100

Table 1. Limits for the RoHS-2 directive. * The bromine content, at the limit concentration of 1000 mg/kg for polybrominated biphenyls and polybrominated diphenylethers, is around 300 mg/kg.

Element	Average concentration (mg/kg)	Certified concentration (mg/kg)	Maximum difference (mg/kg)
Cr	874	886	7.6
Br	499	512	1.8
Cd	113	112	6.2
Hg	516	524	4.1
Pb	323	327	3.4

Table 4. Results of 20 repeated measurements for a PVC sam

Composição mineral

Espectro



Concentração

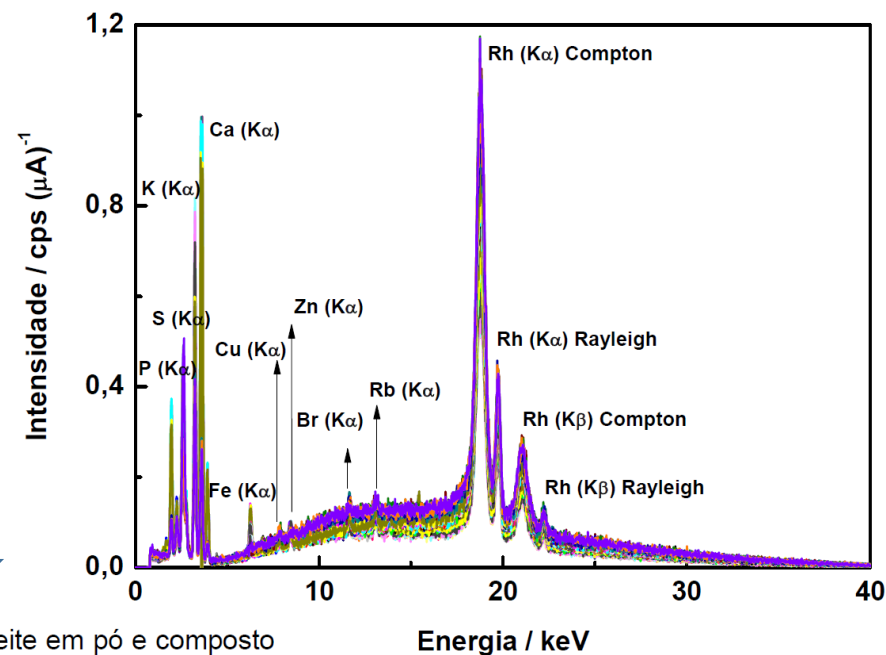


Tabela 6. Faixa de concentração dos elementos detectados nas amostras de leite em pó e composto lácteo a partir da XRF e do método dos FP.

Elemento	K α (keV)	Faixa ($10^{-3} \text{ g kg}^{-1}$)
P	2,01	(33,2 a 157,7) $\times 10^2$
S	2,31	(16,2 a 24,3) $\times 10^2$
K	3,31	(135,7 a 298,1) $\times 10^2$
Ca	3,69	(49,3 a 280,3) $\times 10^2$
Fe	6,40	ND a 308
Cu	8,04	ND a 60
Zn	8,63	ND a 75
Br	11,9	ND a 65
Rb	13,4	ND a 60

ND = Não detectado

G.G. Shimamoto, 2013
Mestrado Unicamp

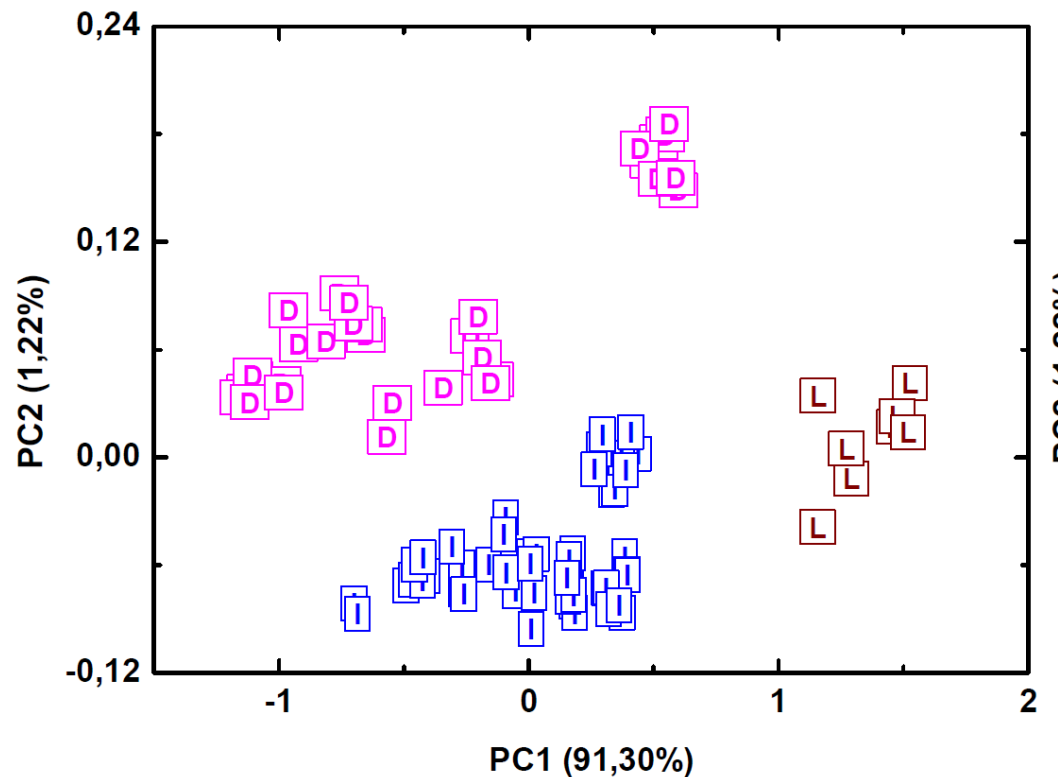


❑ Seria possível distinguir o tipo de leite?

D = Desnatado

I = Integral

L = Composto lácteo



Plantas tratadas com selenato de sódio

Table 2 Concentration of Se (mg kg^{-1}) in selenium-enriched broccoli seedling by benchtop and handheld EDXRF and ICP-MS.

Sample*	Benchtop	Handheld	Recovery (%)***		ICP-MS
			Benchtop	Handheld	
BS0Se14	< LOQ	< LOQ	–	–	0.60 ± 0.06
BS50Se14	163.5 ± 1.0^a	163.9 ± 0.6^a	96	96	170 ± 20^a
BS0Se16	< LOQ	< LOQ	–	–	0.25 ± 0.02
BS50Se16	71.7 ± 0.8^a	73.3 ± 0.4^a	117	119	61 ± 3.1^b
LOD**	0.9	0.6	–	–	0.07
LOQ**	3.0	2.1	–	–	0.21

*Seedlings of broccoli treated with distilled water (BS0Se14) and sodium selenate (BS50Se14) cultivated in August–October 2014; Seedlings of broccoli treated with distilled water (BS0Se16) and sodium selenate (BS50Se16) cultivated in August–October 2016

**Limits of detection (LOD) and quantification (LOQ) (mg kg^{-1})

***EDXRF systems recoveries (%) compared to ICP-MS

^aThe same letter in the same row means no significant differences among the values ($p < 0.05$)

Each value is expressed as the mean \pm one standard deviation (SD)

Food Analytical Methods (2019) 12:1520–1527
<https://doi.org/10.1007/s12161-019-01489-5>

Benchtop and Handheld Energy-Dispersive X-Ray Fluorescence (EDXRF) as Alternative for Selenium Concentration Measurement in Biofortified Broccoli Seedling

Patricia Bachiega¹ • Eduardo de Almeida² • Jocelém Mastrodi Salgado¹ • Marco Aurelio Zezzi Arruda^{3,4} • Eraldo Luiz Lehmann^{3,4} • Maressa Caldeira Morzelle⁵ • Hudson Wallace Pereira de Carvalho²



Variantes da fluorescência de raios X dispersiva em energia: microanálise por fluorescência de raios X e fluorescência de raios X em regime de reflexão total

Prof. Hudson W.P. Carvalho

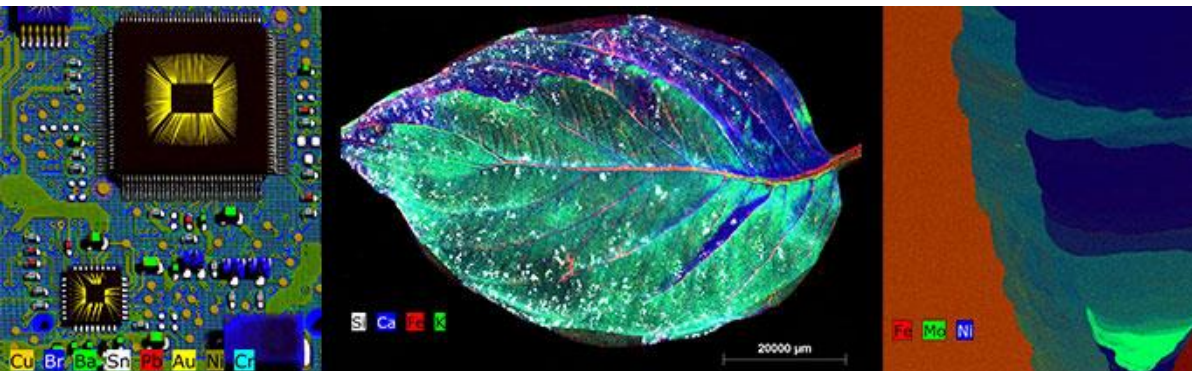
Universidade de São Paulo

Centro de Energia Nuclear na Agricultura



- Revisão do fenômeno de fluorescência de raios X**
- Detectores dispersivos de energia**
- Microanálise por fluorescência de raios X**
- Fluorescência de raios X em regime de reflexão total**

Mapas microquímicos

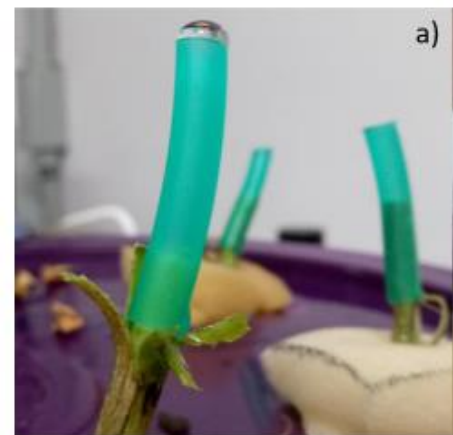


<https://www.blue-scientific.com/micro-xrf-workshop/>

Quando o volume/massa é limitado

R.G. Lima, 2020

Spectrochimica Acta Part B 59 (2004) 1251–1257



seiva



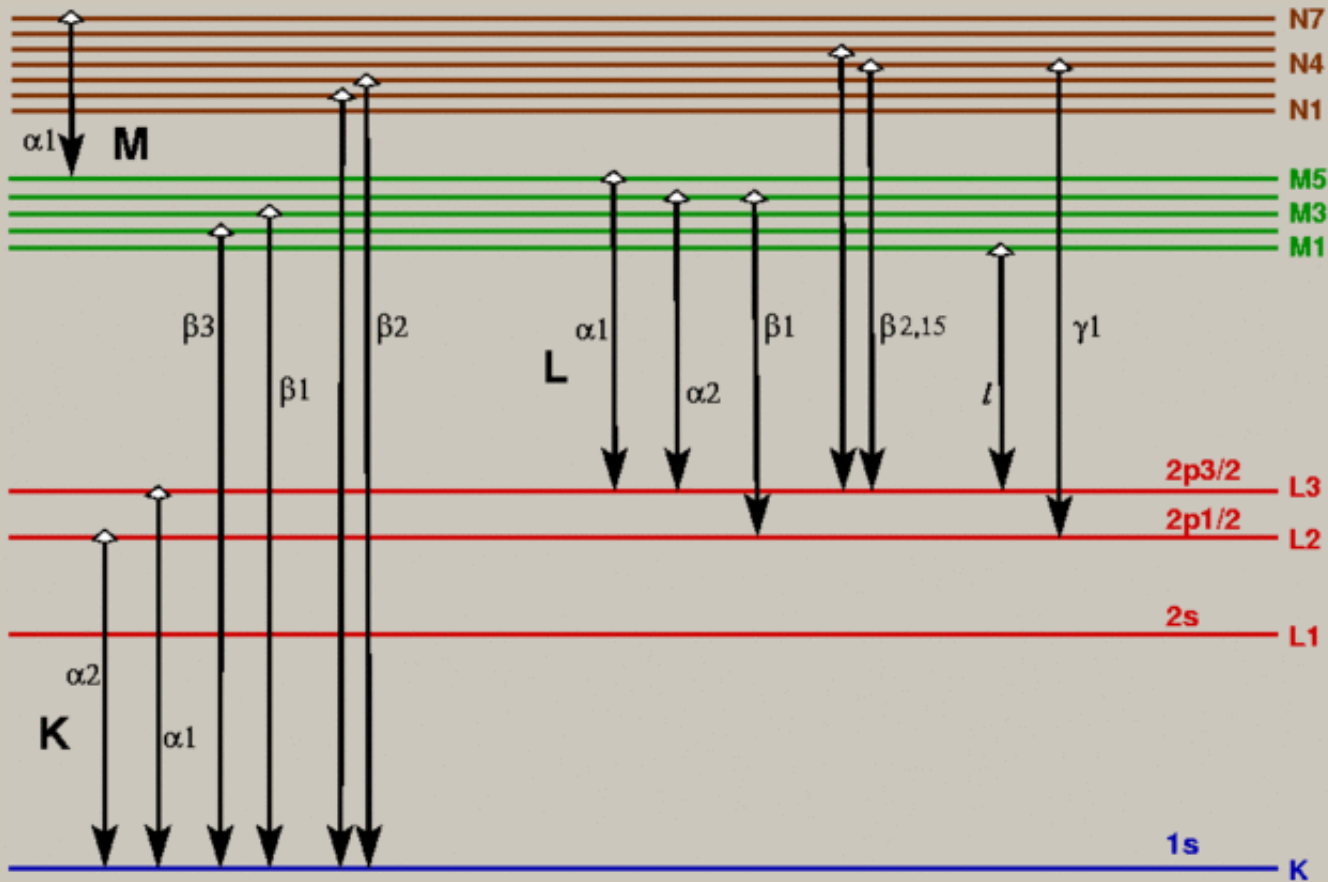
Artefatos arqueológicos

Breve Revisão:

- 1. Fenômeno de fluorescência de raios X**
- 2. Detectores dispersivos de energia**

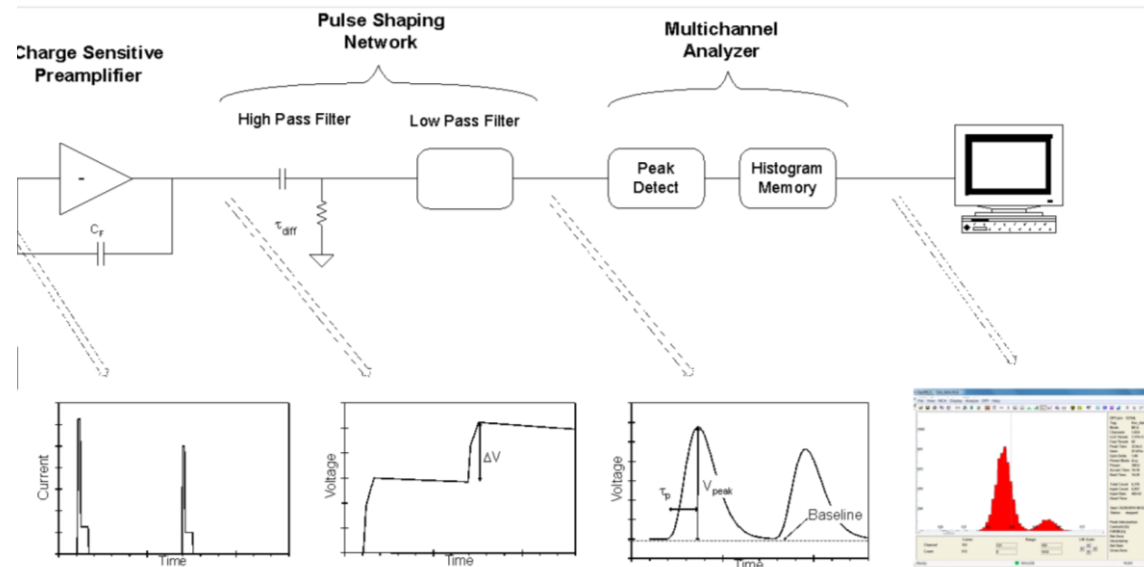
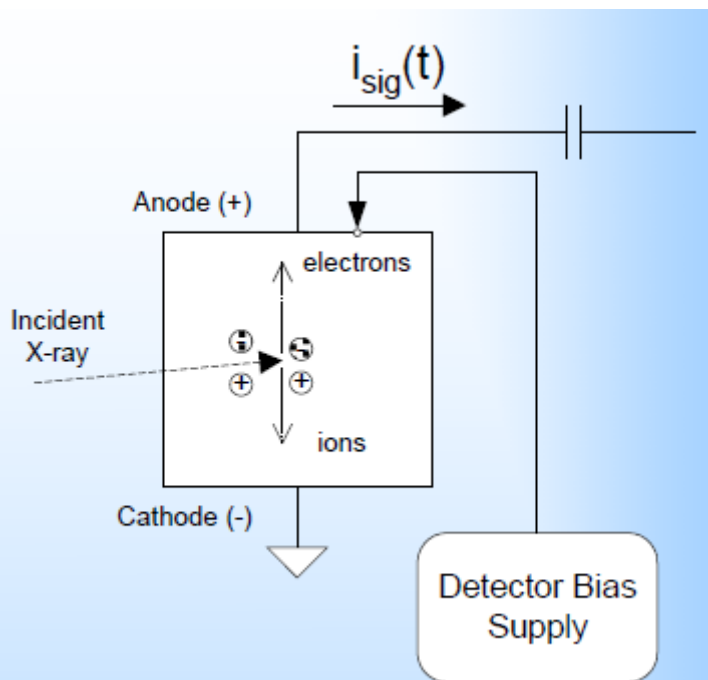
Fluorescência de raios X

Electronic Transitions of the Emission Lines for Any Element



❑ Proporcional a gás , resolução na faixa de 800 eV

❑ Semicondutor, Si(Li) (R *ca.* 170) ou SDD (R *ca.* 125 eV)



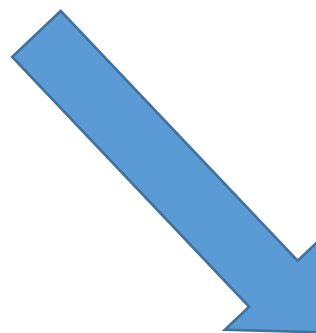
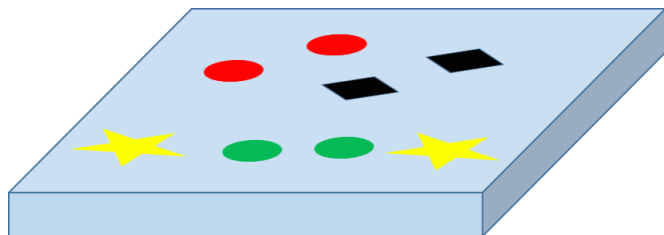
Microanálise por fluorescência de raios X



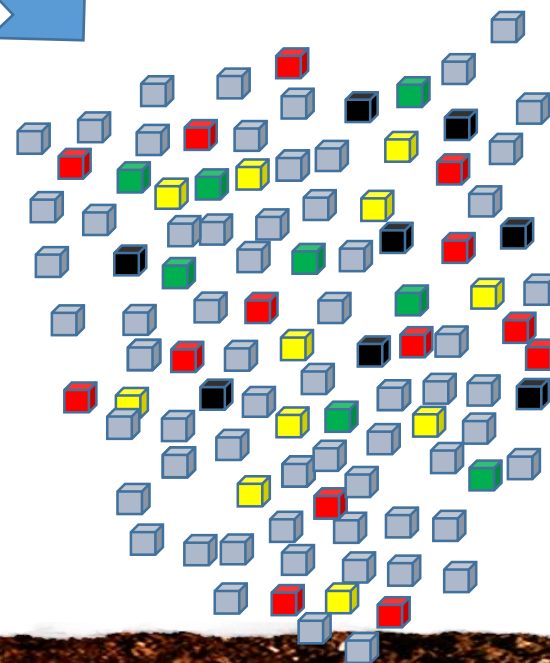
- ❑ O que se busca na microanálise?
- ❑ Como produzir microfeixes de raios X
- ❑ Principais parâmetros das análises
- ❑ Exemplos de aplicações

Determinação elementar

Amostra heterogênea



Amostra homogênea

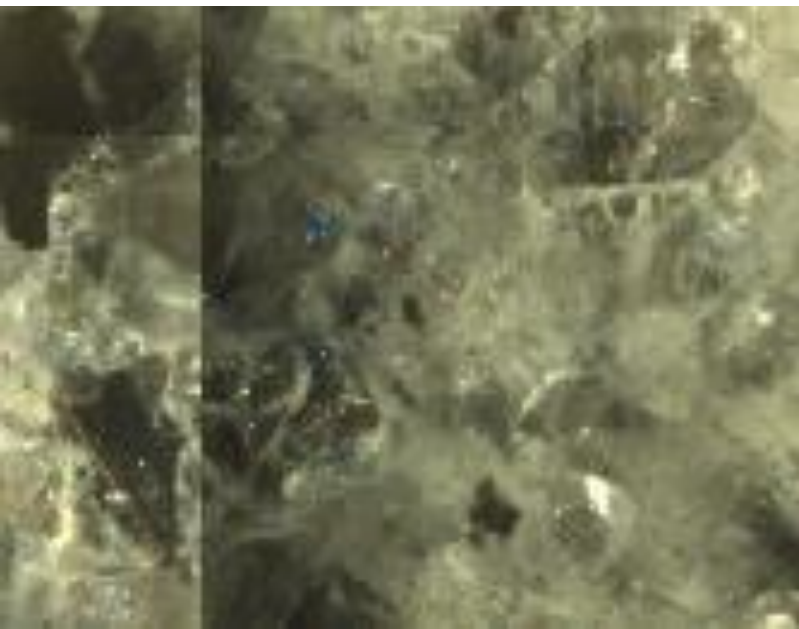


□ Normalmente o analista se interessa pela concentração média dos elementos na amostra homogeneização da amostra

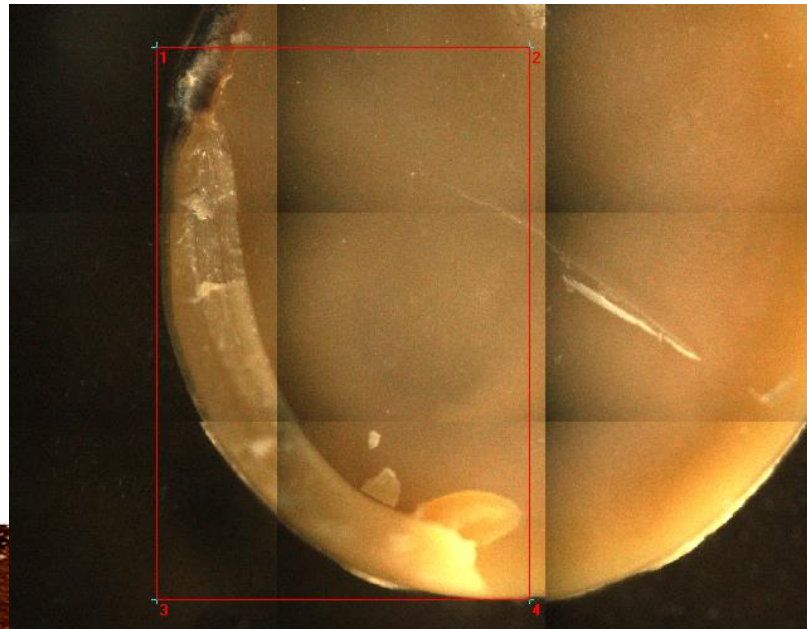
□ Nesse caso, a determinação elementar é precedida pela homogeneização da amostra

- A microanálise se interessa pela heterogeneidade
- Por padrões de distribuição espacial estáticos ou dinâmicos
- Concentrações locais ao invés de médias

Granito

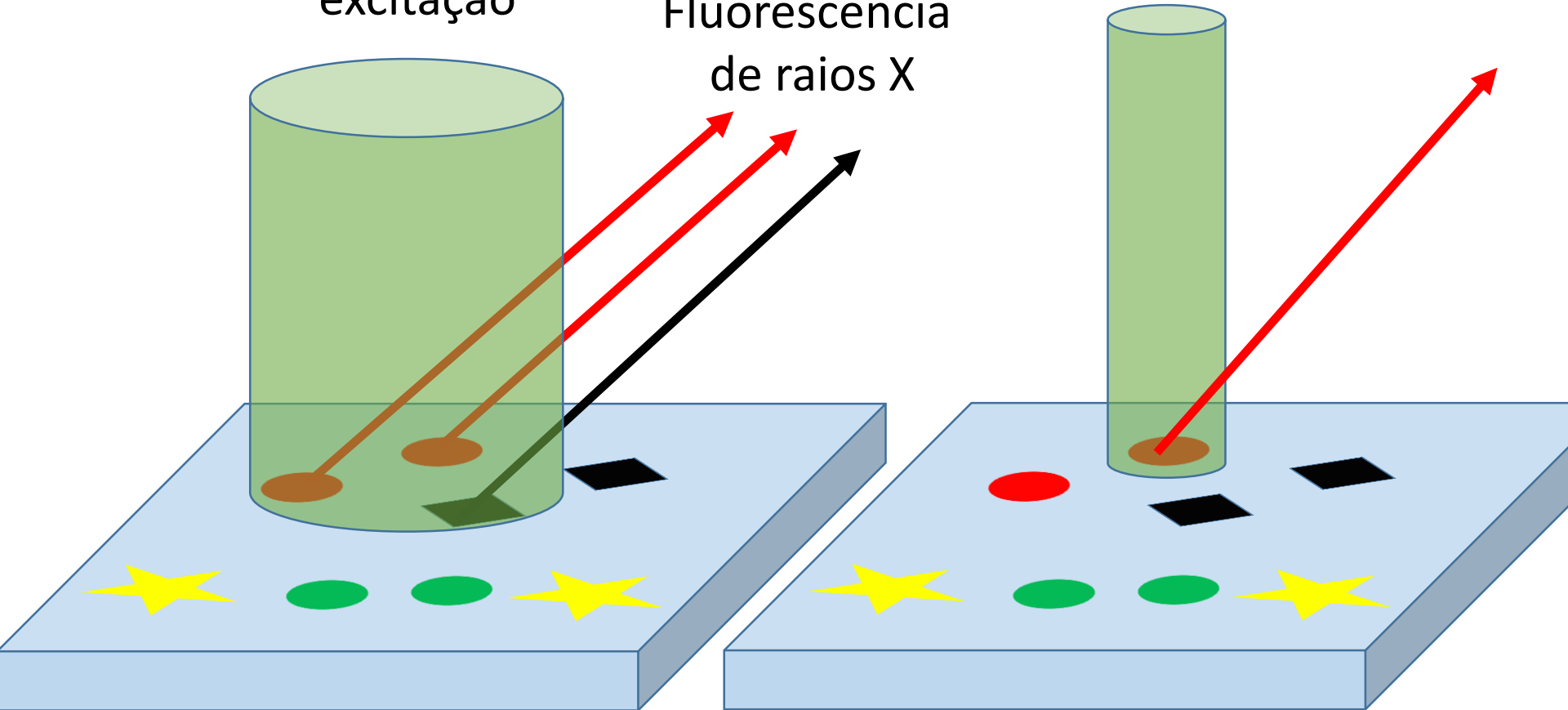


Semente de soja



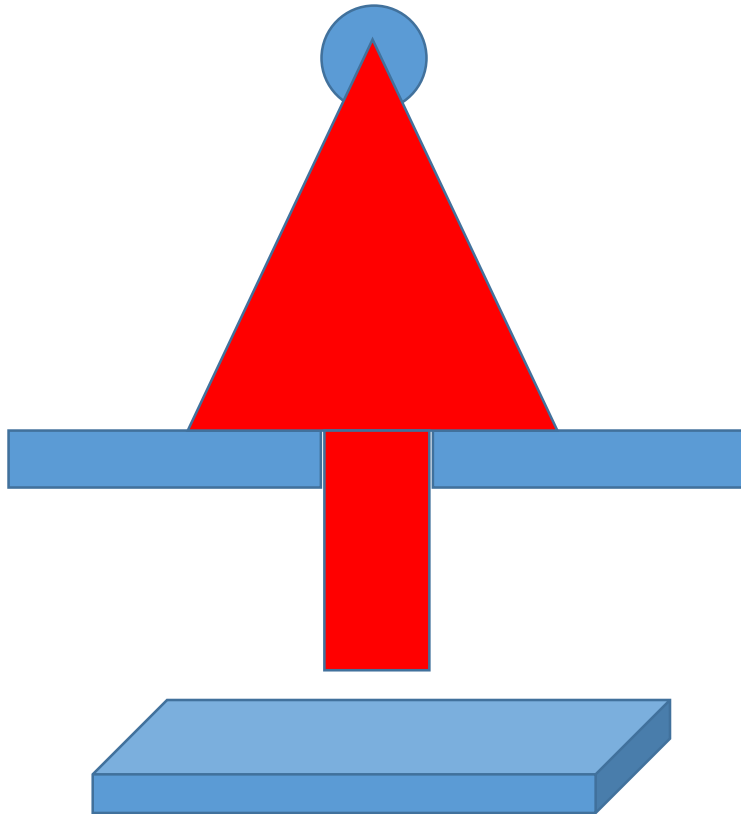
Feixe de
excitação

Fluorescência
de raios X



☐ Fendas e *pinholes*

Fonte de raios X

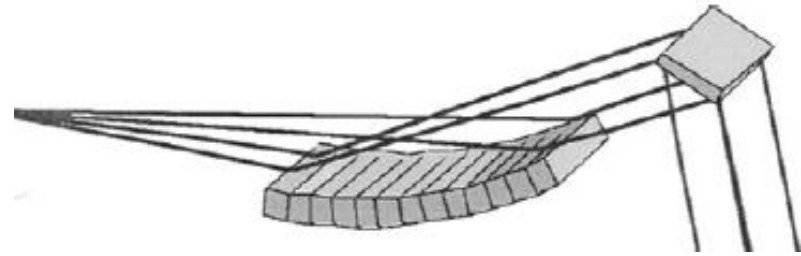
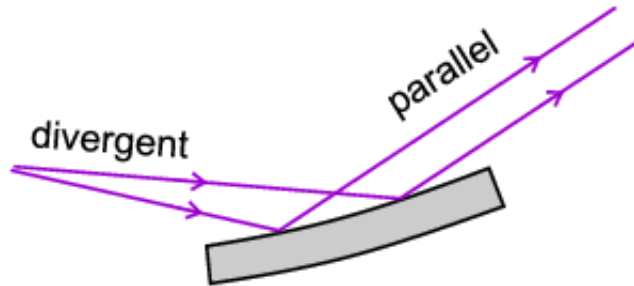


Aperture



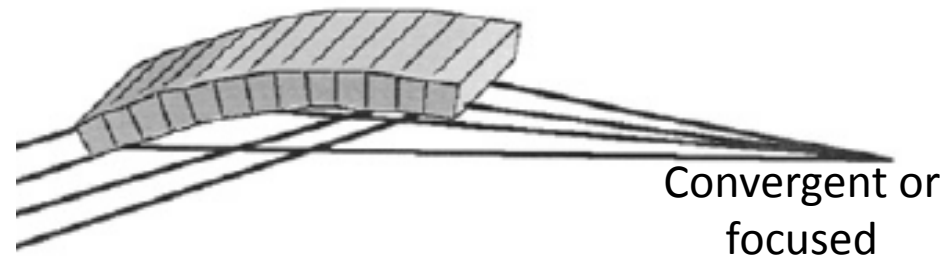
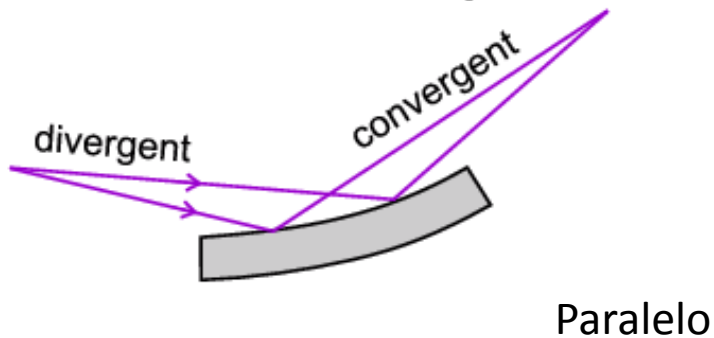
Minimum diameter	About 10 μm
Beam collimation	Almost parallel
Beam intensity	Very low
Cost	Low

□ Espelhos colimadores



Colimação e rejeição de harmônicos

□ Espelhos convergentes



Capilares

Pense em um espelho 3D

DESIGN OF SINGLE-BOUNCE MONOCAPILLARY X-RAY OPTICS

Sterling Cornaby², Thomas Szebenyi¹, Rong Huang³ and Donald H Bilderback^{1,2}

¹Cornell High Energy Synchrotron Source (CHESS)

²School of Applied and Engineering Physics, Cornell University

³Advanced Photon Source (APS), Argonne National Laboratory

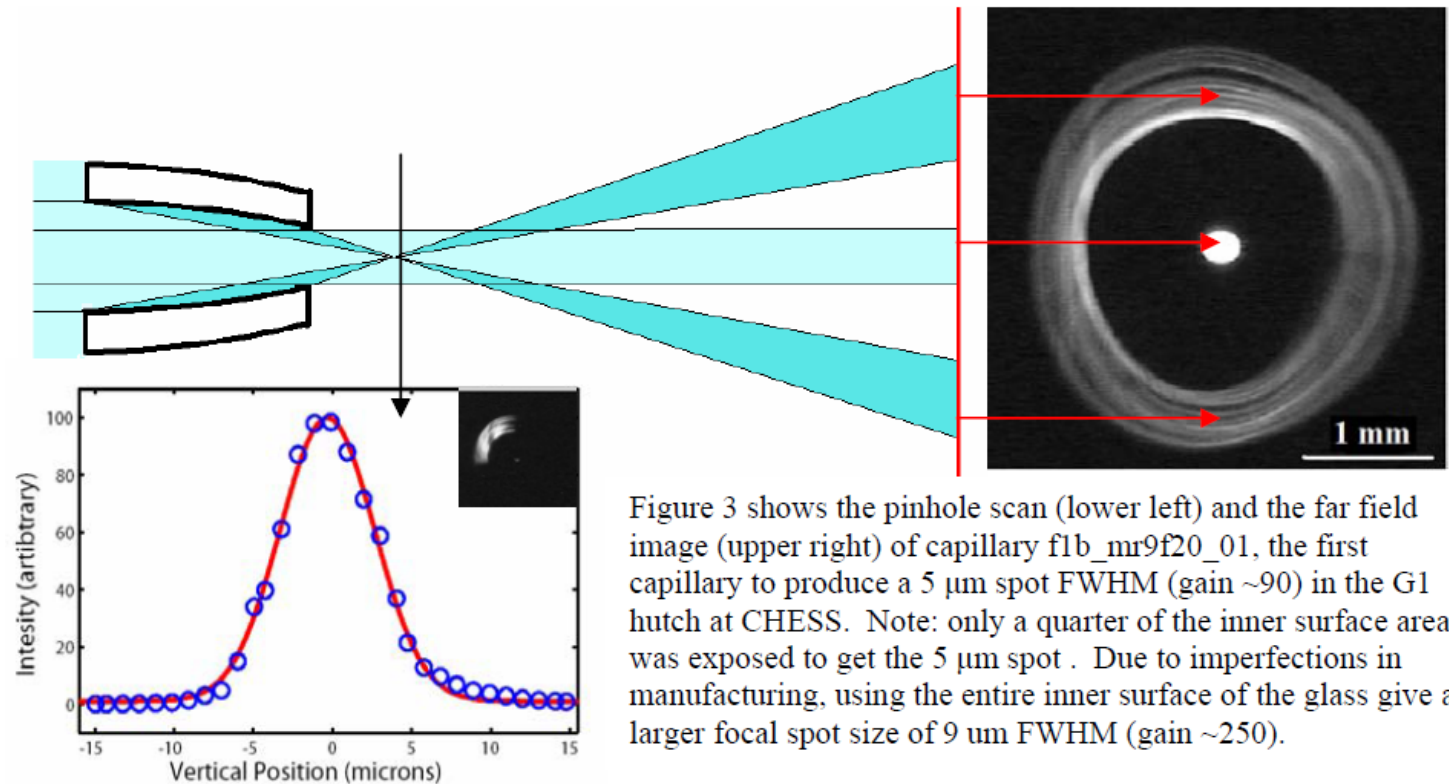


Figure 3 shows the pinhole scan (lower left) and the far field image (upper right) of capillary f1b_mr9f20_01, the first capillary to produce a 5 μm spot FWHM (gain ~ 90) in the G1 hutch at CHESS. Note: only a quarter of the inner surface area was exposed to get the 5 μm spot. Due to imperfections in manufacturing, using the entire inner surface of the glass give a larger focal spot size of 9 μm FWHM (gain ~ 250).

ca. U\$ 200 k

Sem preparo

Corte

Polimento

Emblocagem

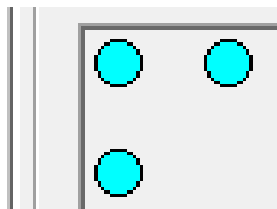


Parâmetros instrumentais

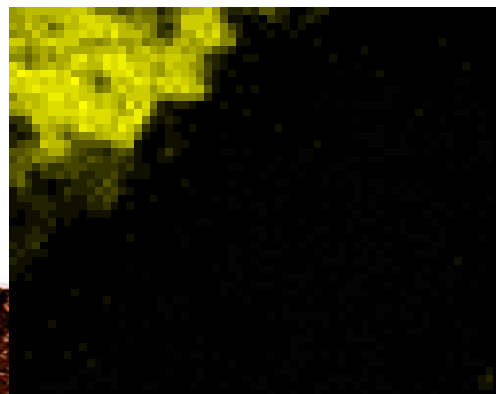
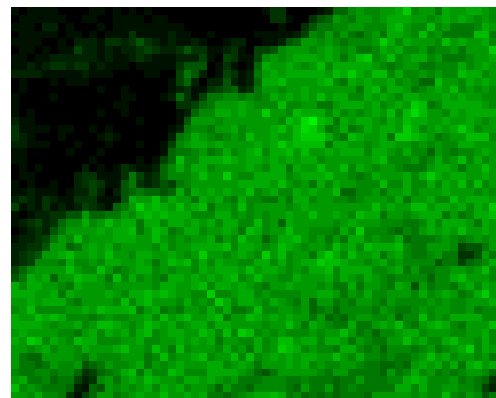
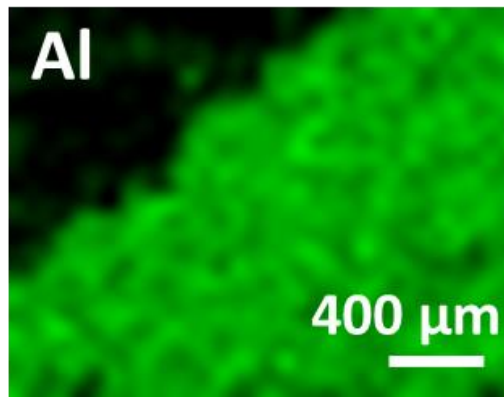
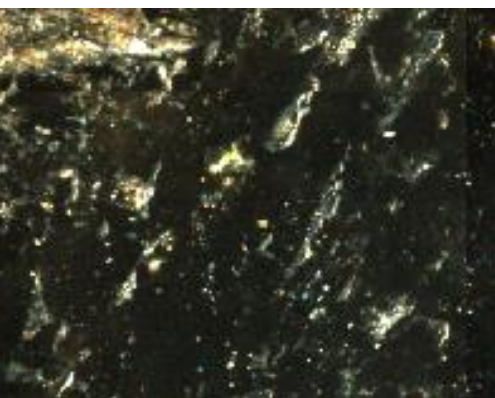
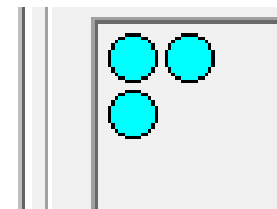
❑ Corrente, tensão, tempo de aquisição, vácuo?, filtro?

❑ Resolução lateral

X beam spacing: 69 μm
Y beam spacing: 69 μm



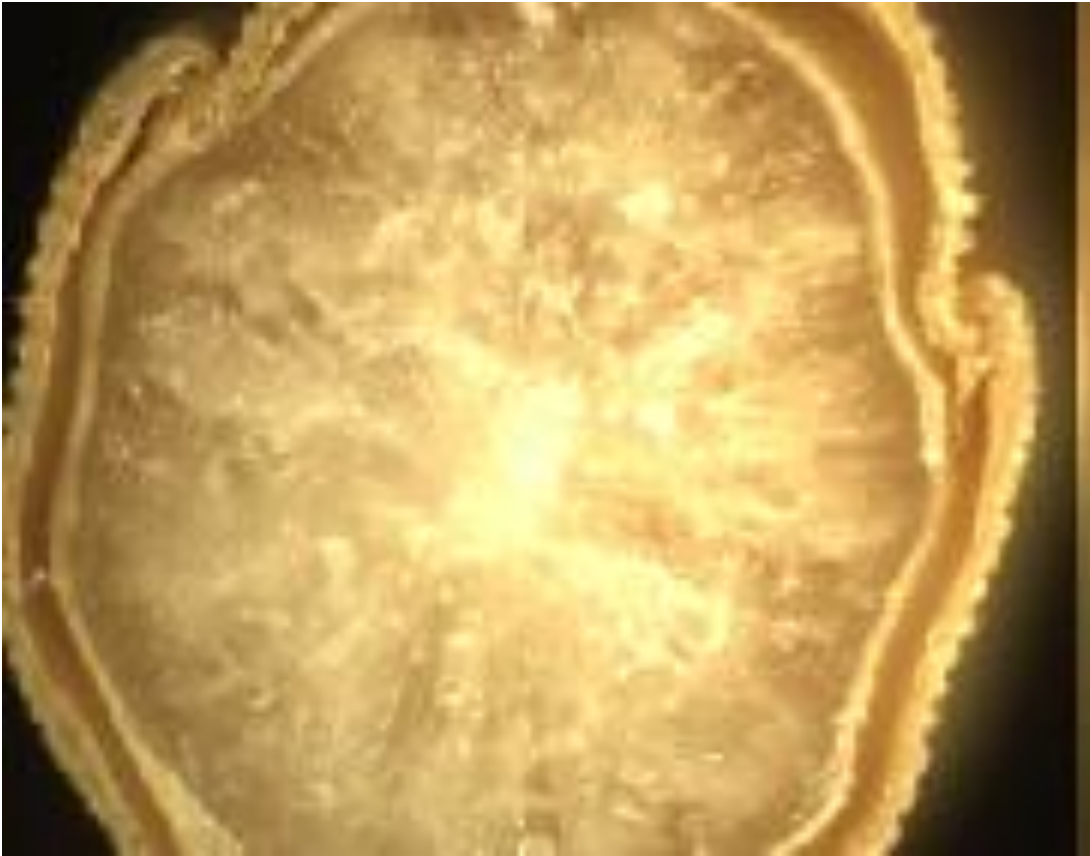
X beam spacing: 34 μm
Y beam spacing: 34 μm



Exemplo de Aplicação de microanálise por XRF



Arroz



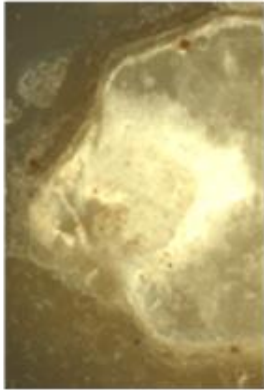
Arroz

https://www.123rf.com/photo_70257410_close-up-of-white-polished-rice-grain.html

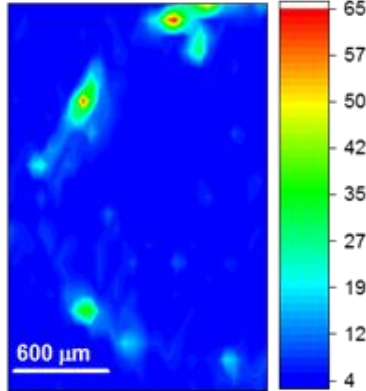


Arroz

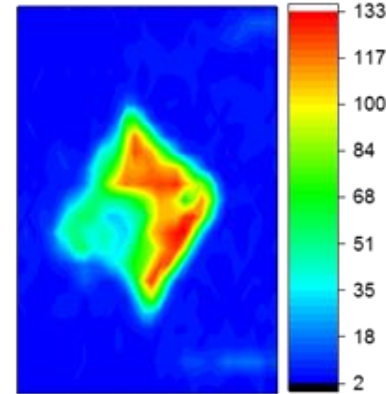
A



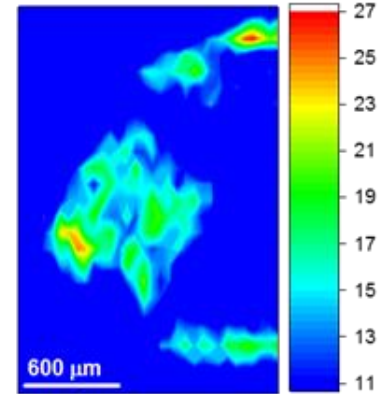
Si K α Net Counts



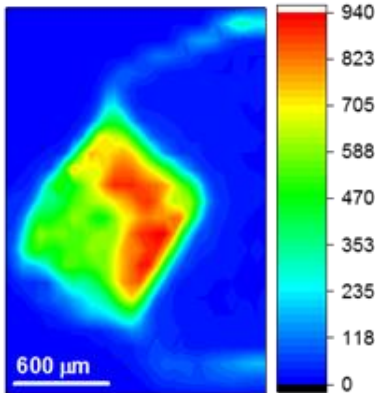
P K α Net Counts



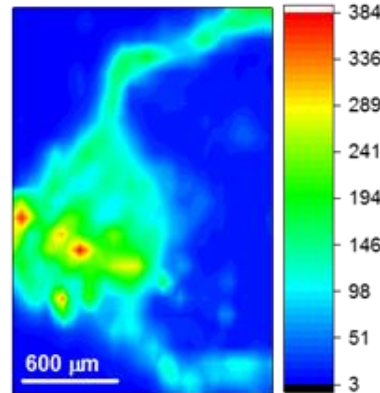
S K α Net Counts



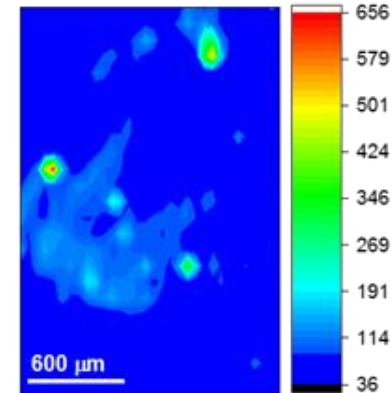
K K α Net Counts



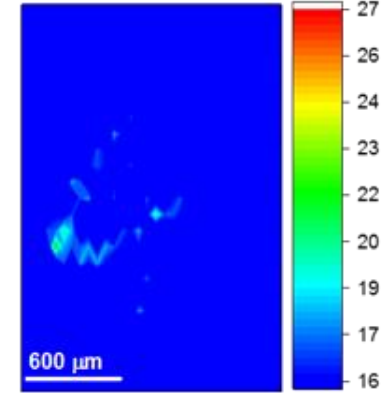
Ca K α Net Counts



Fe K α Net Counts

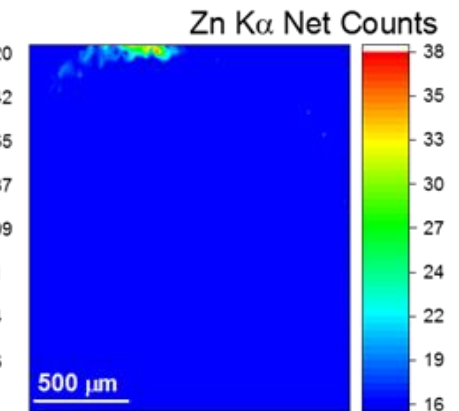
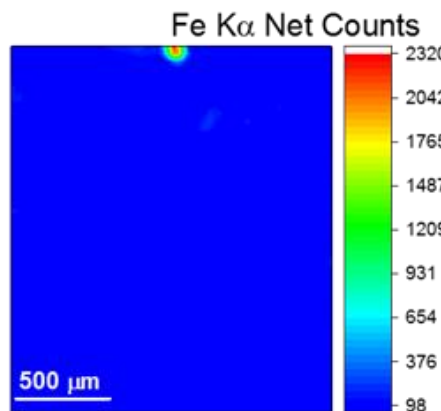
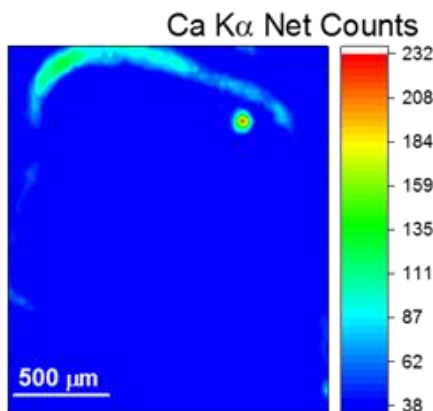
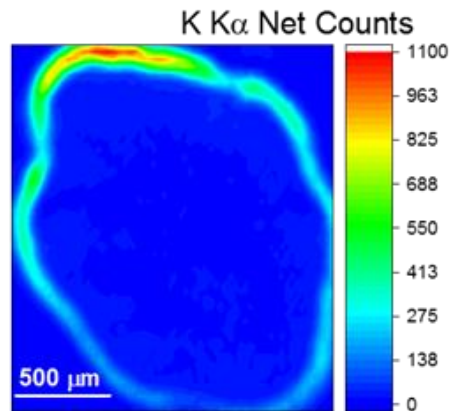
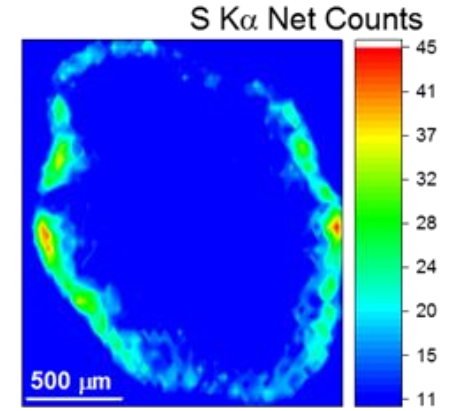
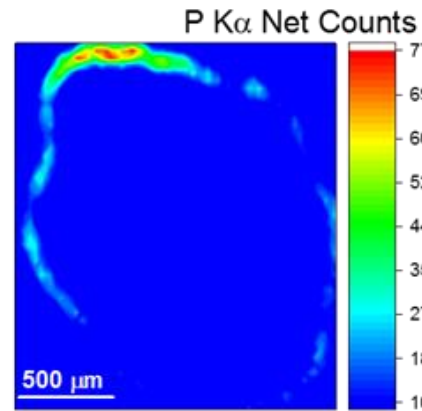
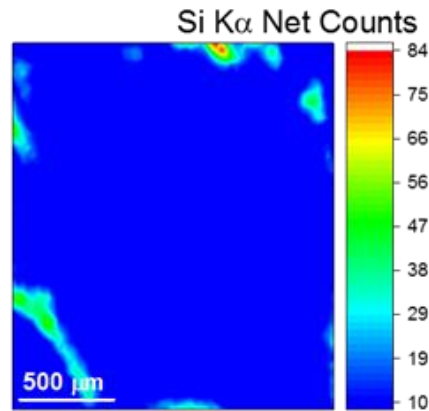
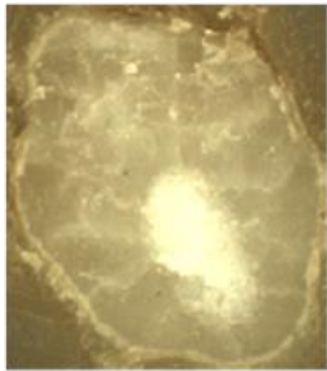


Zn K α Net Counts

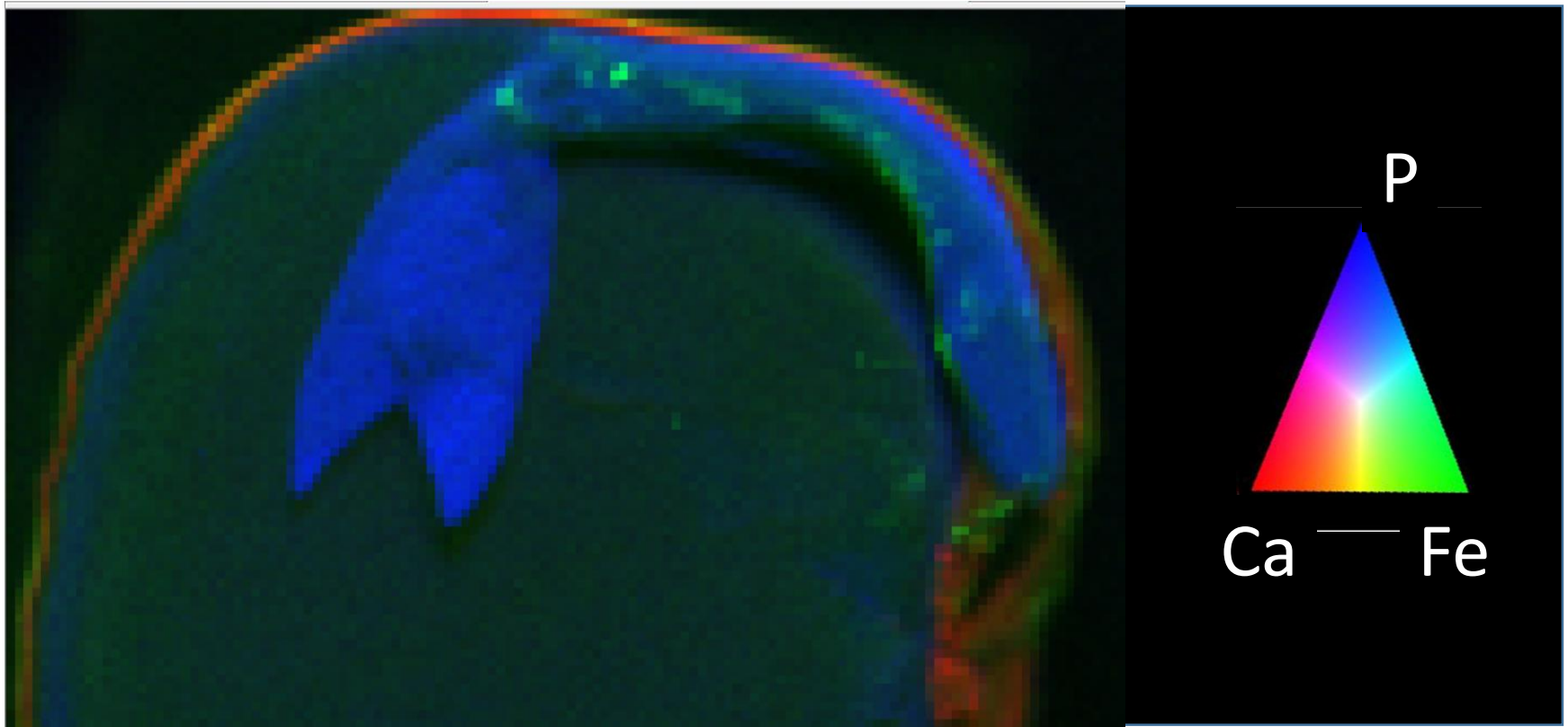


Arroz

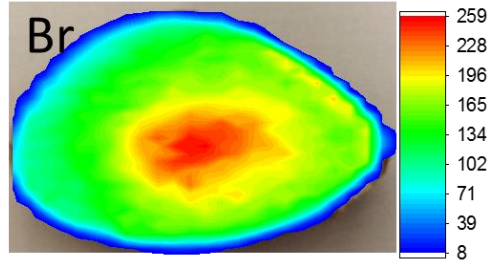
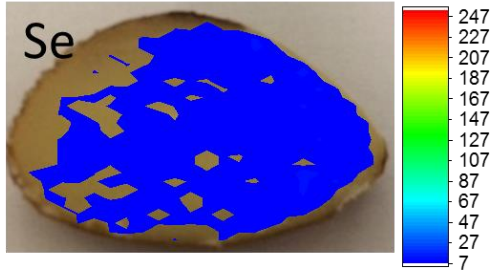
B



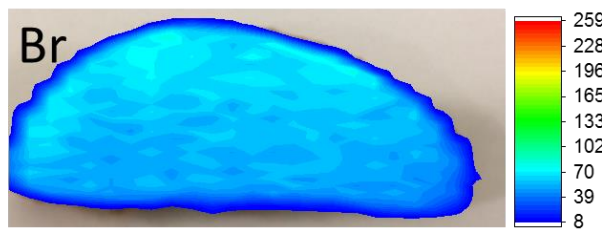
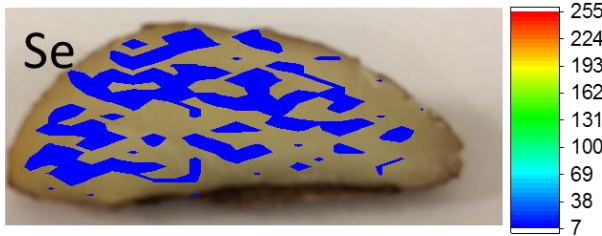
Arroz



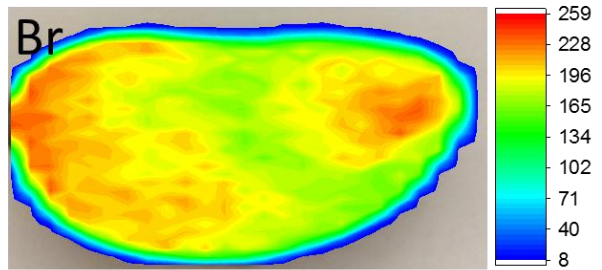
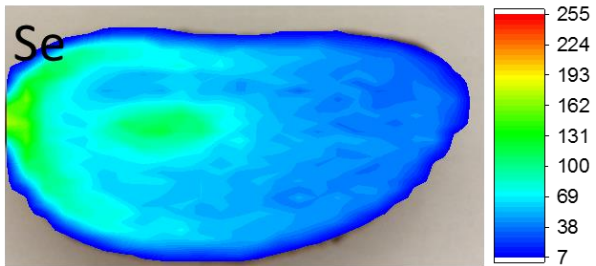
Roraima



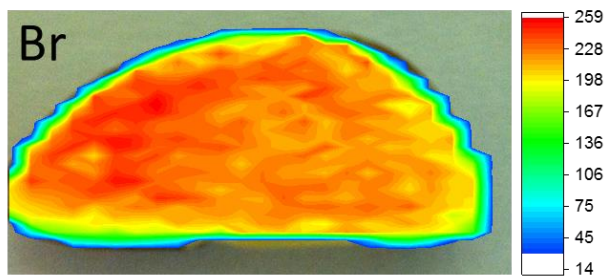
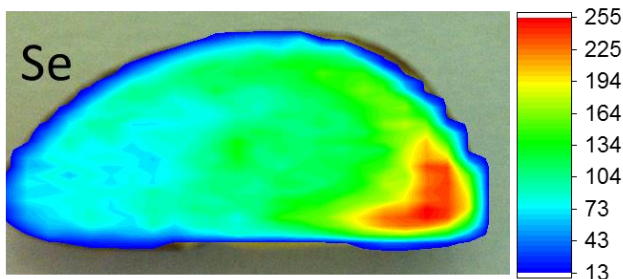
Acre



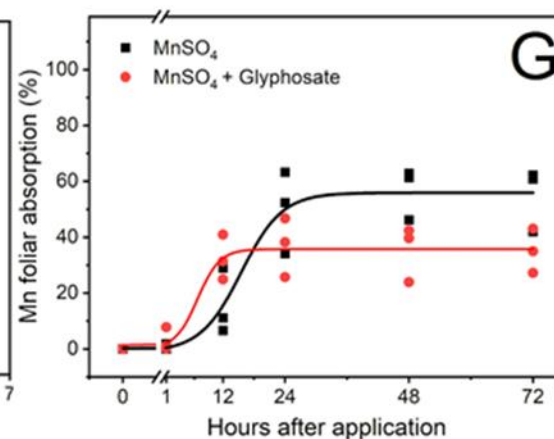
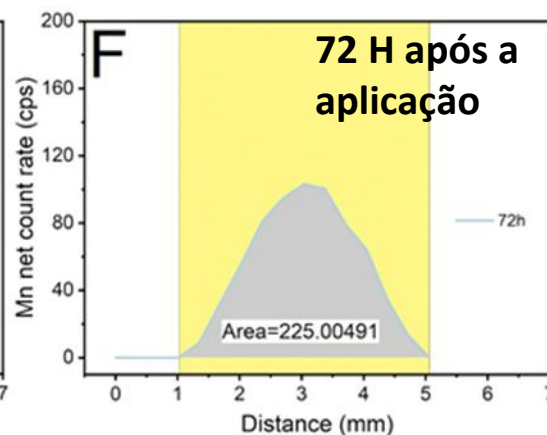
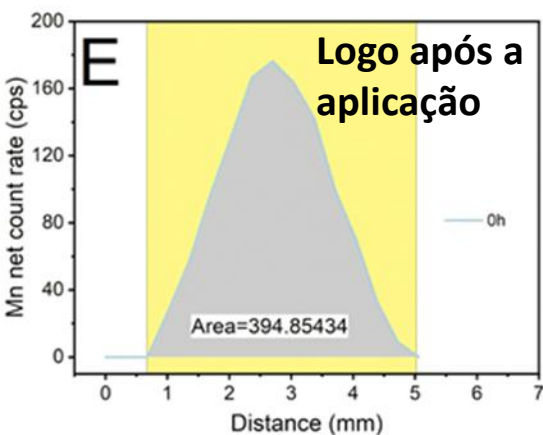
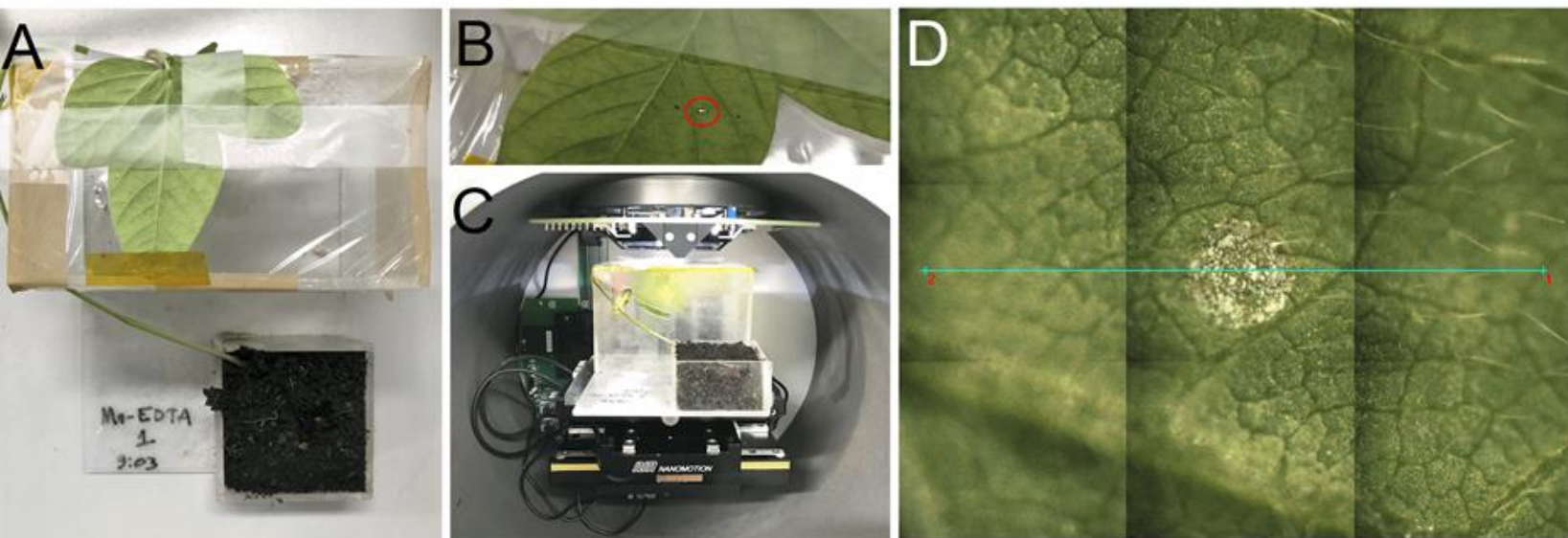
Amazonas



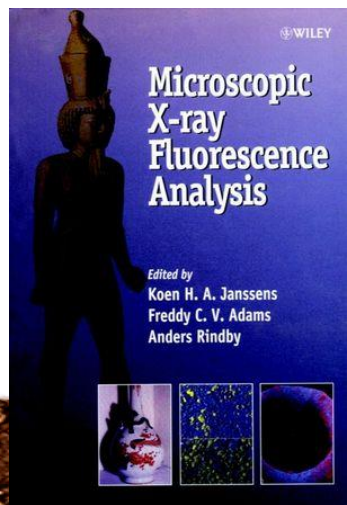
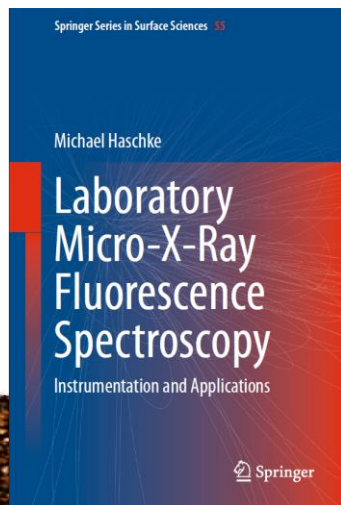
Amapá



Absorção e transporte de fertilizantes



- ❑ Adequada para a investigação de heterogeneidades
- ❑ Análises pontuais, em linha ou bidimensionais
- ❑ Resolução lateral da ordem de milímetros a nanômetros
- ❑ Resultados qualitativos e quantitativos
- ❑ Mais comum em síncrotron, mas vem se popularizando em laboratórios



Laboratory Microprobe X-Ray Fluorescence in Plant Science: Emerging Applications and Case Studies

Eduardo S. Rodrigues¹, Marcos H. F. Gomes¹, Nádía M. Duran¹, João G. B. Cassanji¹, Tatiana N. M. da Cruz¹, Analdar Sant'Anna Neto², Susilaine M. Savassa¹, Eduardo de Almeida¹ and Hudson W. P. Carvalho^{1*}

¹ Nuclear Instrumentation Laboratory, Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, Brazil, ² Physiology of Trees Laboratory, Department of Forest Science, College of Agriculture Luiz de Queiroz, University of São Paulo, Piracicaba, Brazil

Fluorescência de raios X em regime de reflexão total



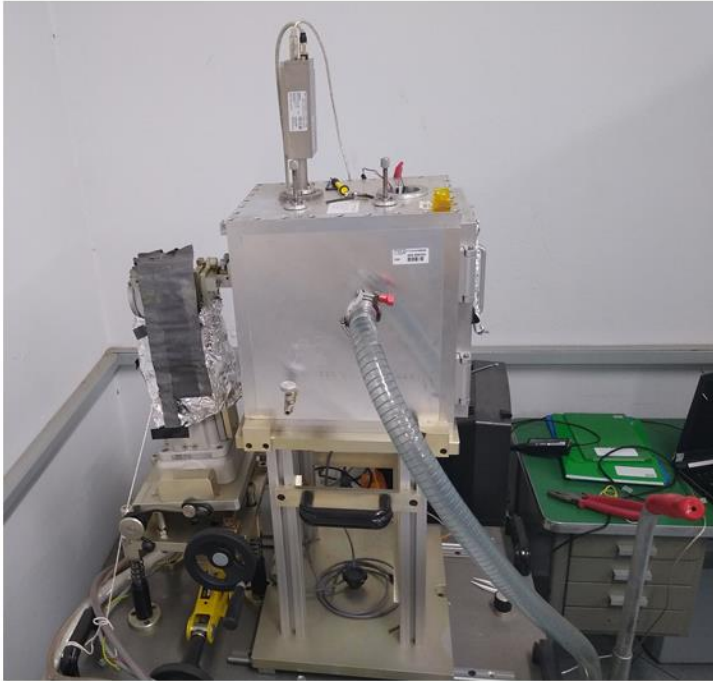
- Características analíticas da TXRF
- O que é reflexão total?
- Por que a TXRF oferece baixos LODs?
- Preparo de amostras
- Exemplos de aplicações



- Baixos limites de detecção – $\mu\text{g L}^{-1}$ ou $\mu\text{g kg}^{-1}$
- Preparo de amostra simples, geralmente não requer digestão
- Emprega pequeno volume/massa de amostra – dezenas de μL ou mg
- Alta frequência analítica (*ca.* 60-300 s por amostra)



Lab-made



Bruker

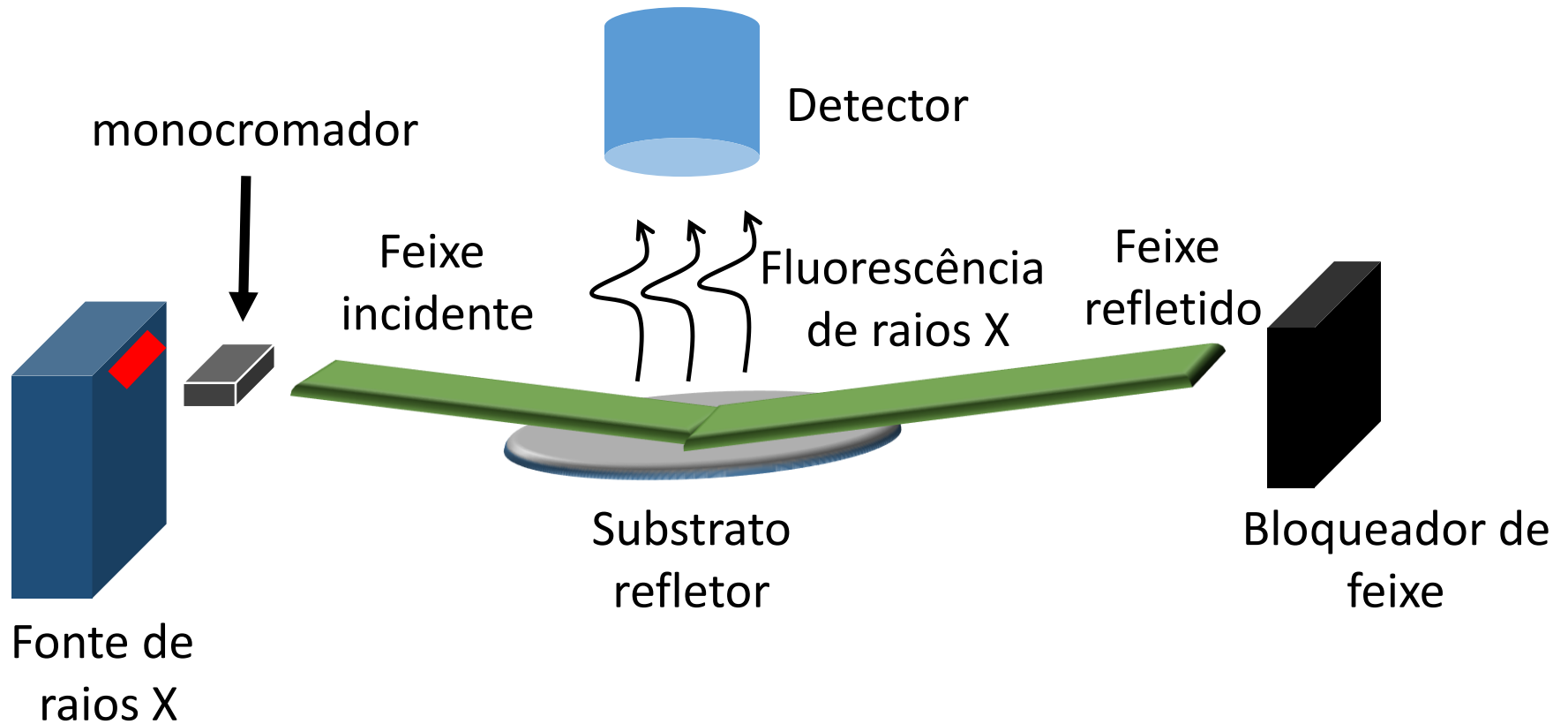


US\$ 100 k

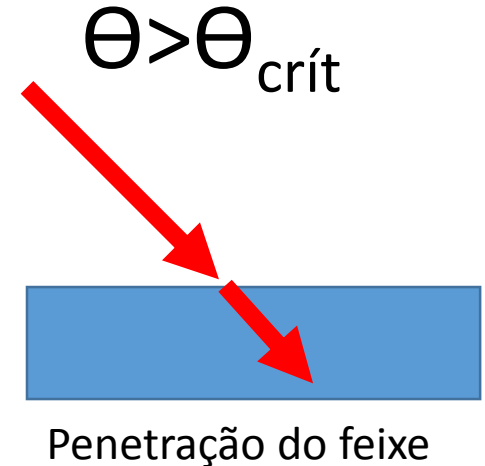
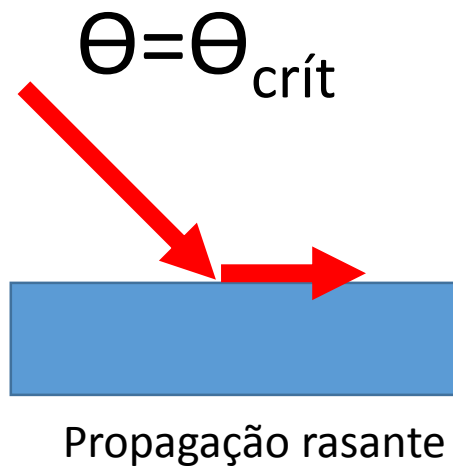
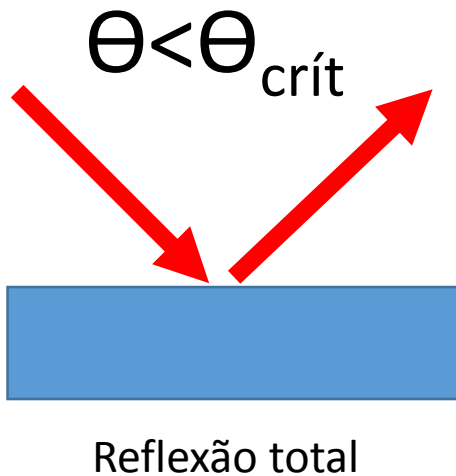
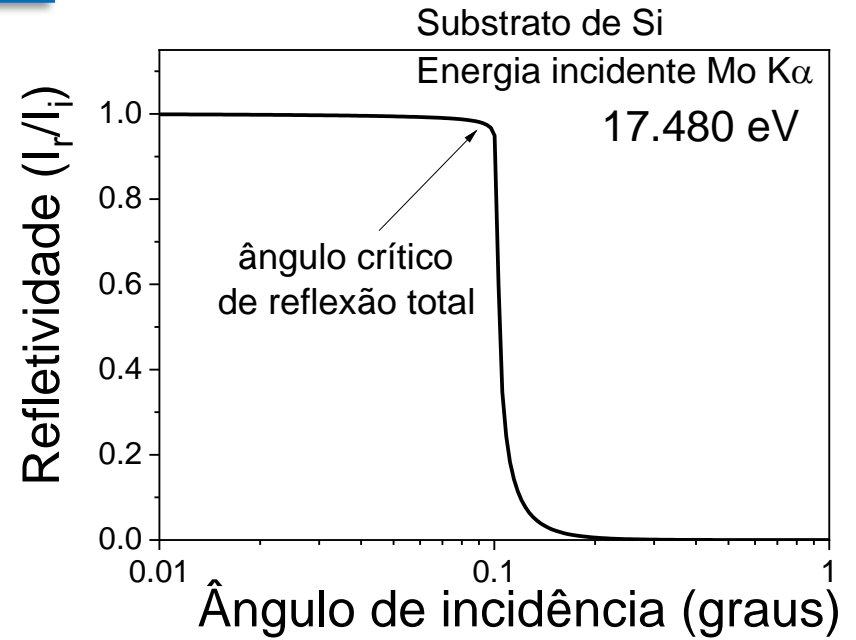
1 Mg de soja ca. US\$ 600

1 Picofox ~ 167 toneladas de soja

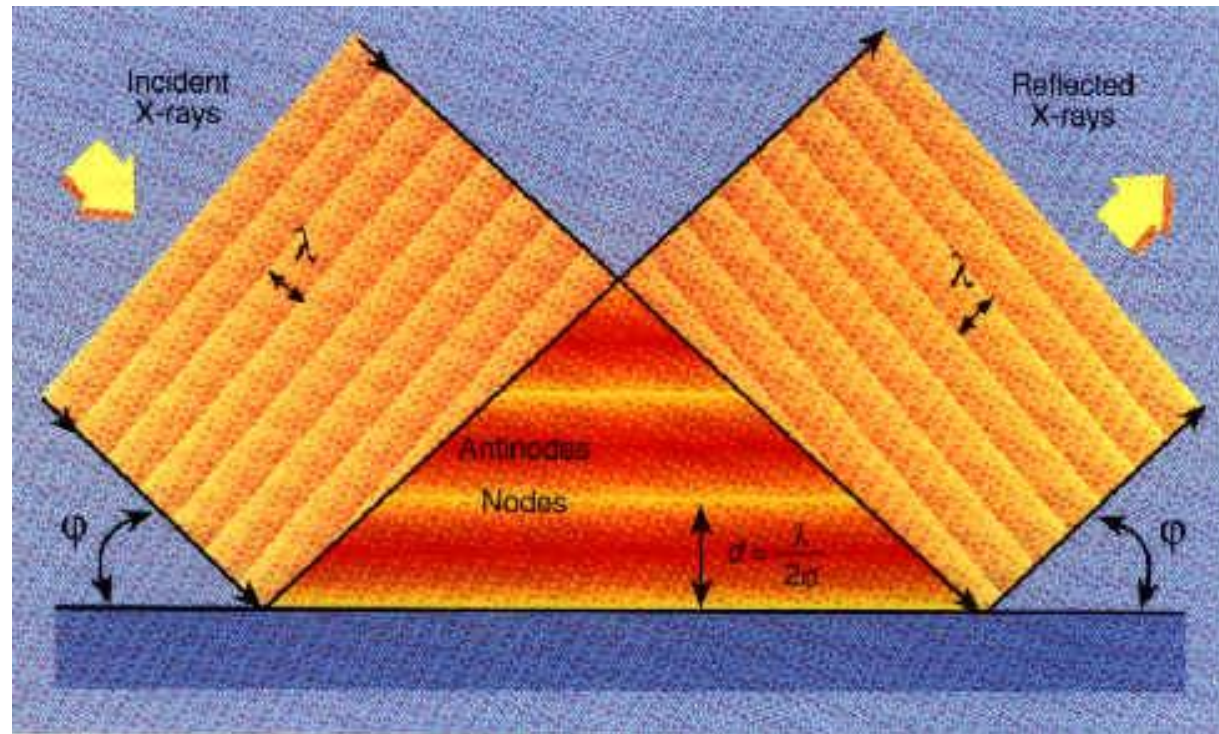
Equipamento



Reflexão externa total



- Abaixo do $\theta_{\text{crítico}}$ forma-se um campo de ondas estacionárias na superfície do substrato

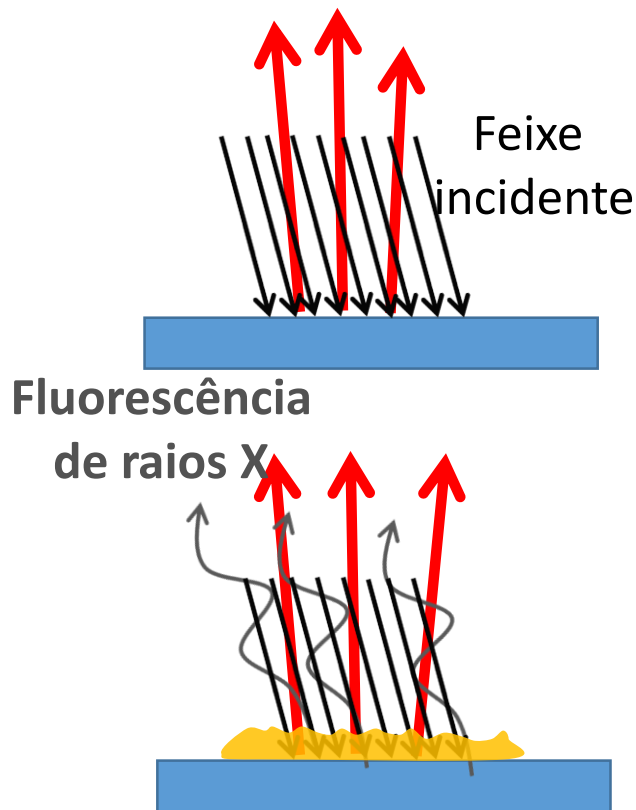


TXRF versus geometria convencional

Amostra: líquidos ou sólidos

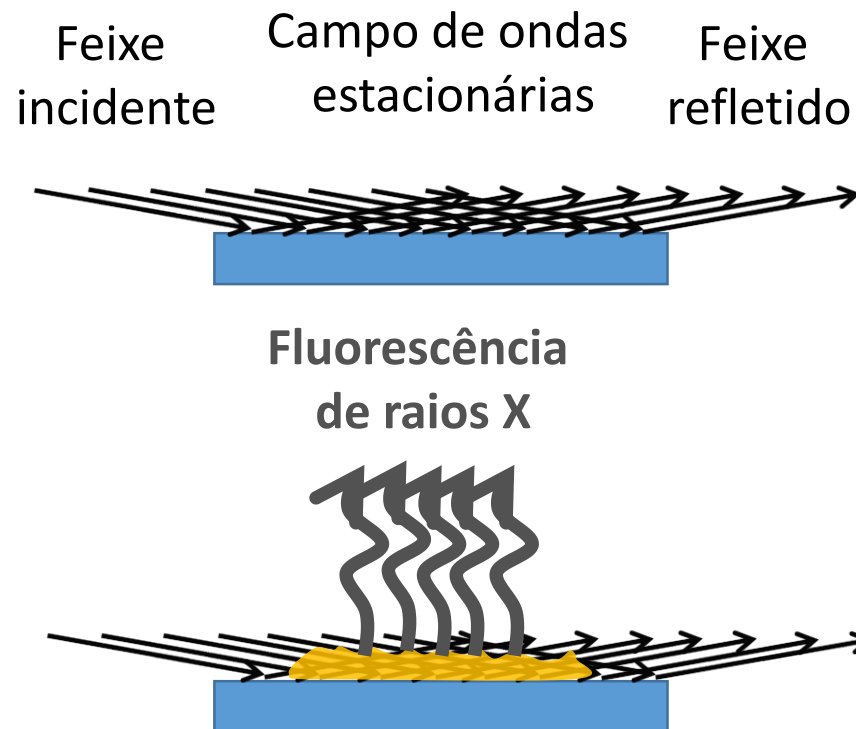
Radiação restroespalhada e fluorescência de raios X do substrato

EDXRF

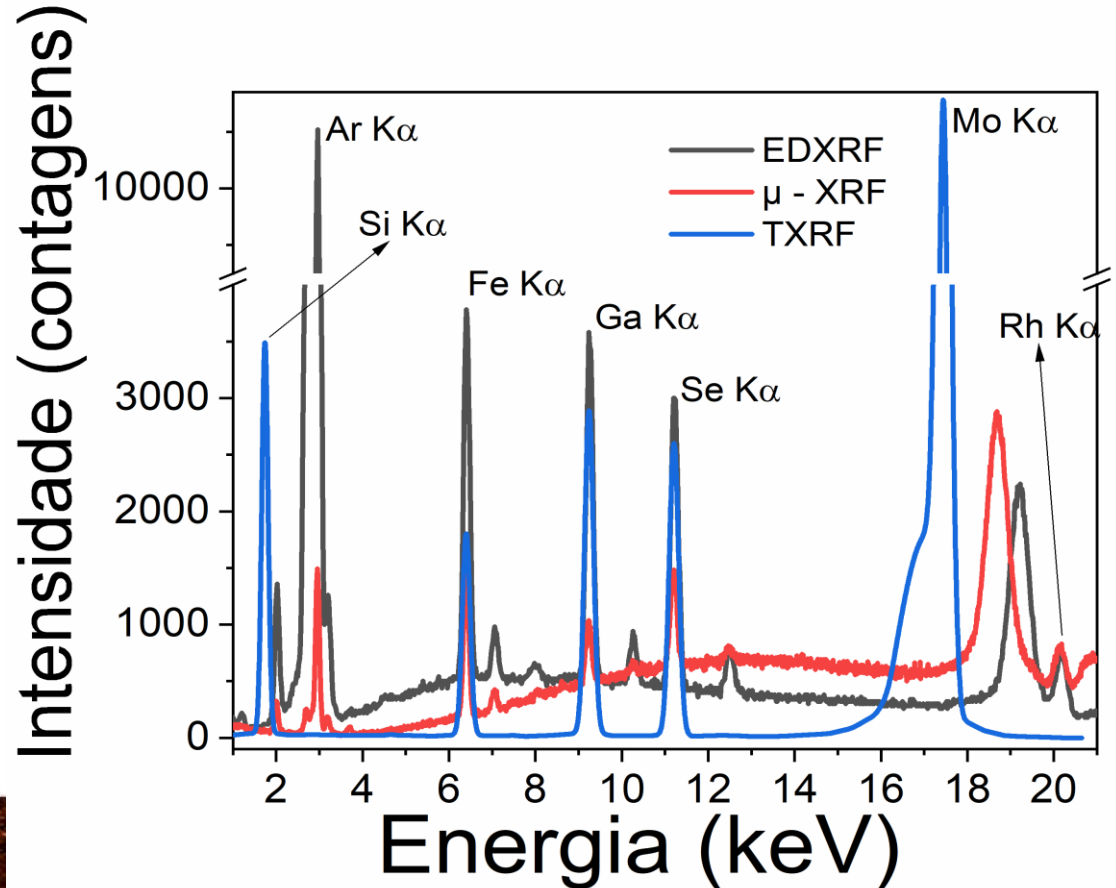


Substrato refletor

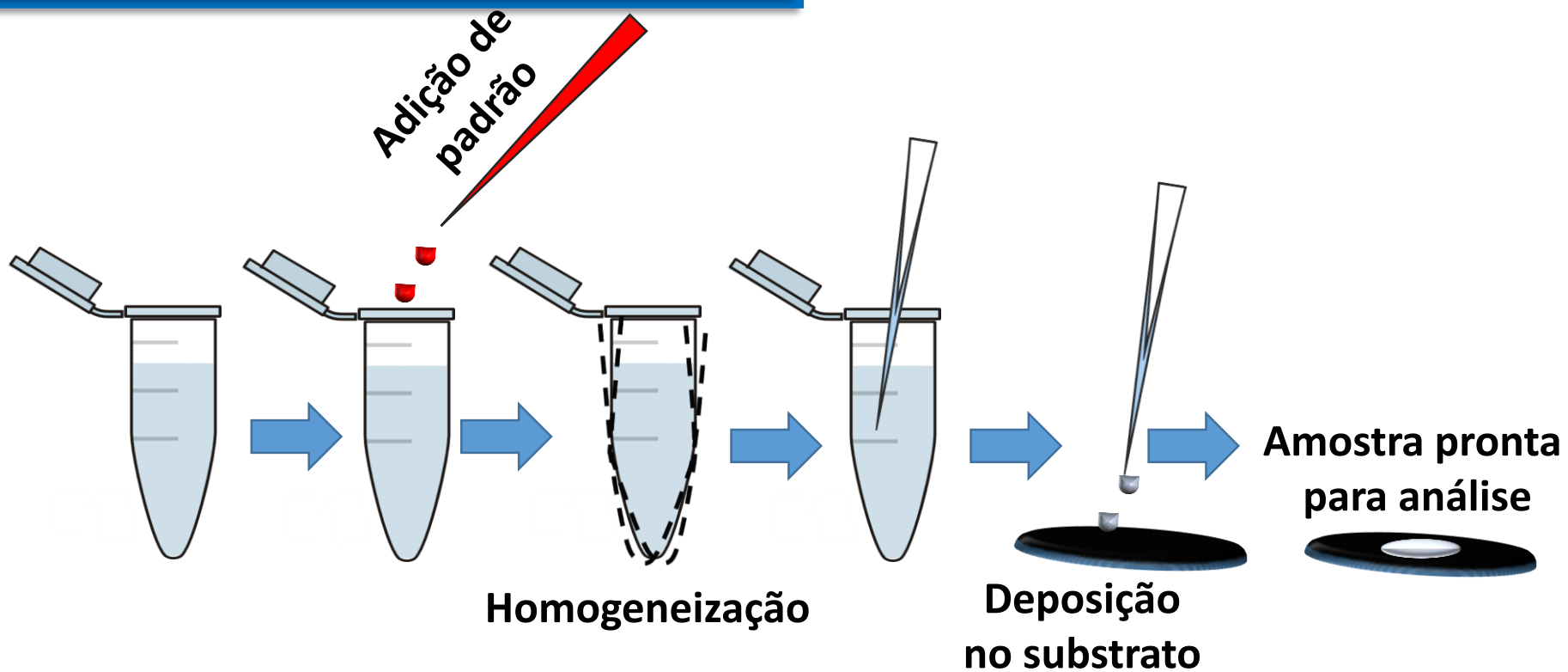
TXRF



Espectros registrados em diferentes geometrias

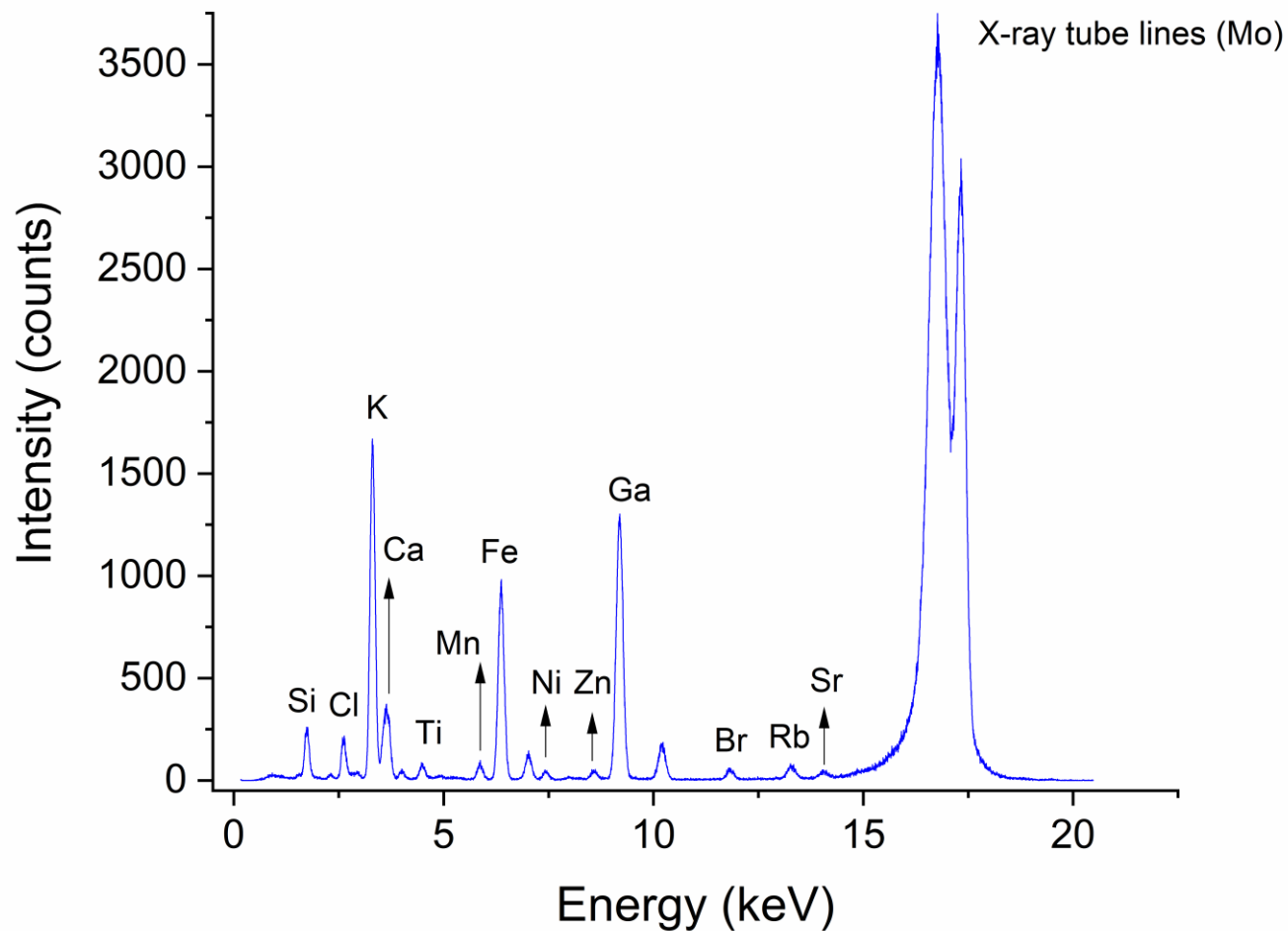


Preparo de amostra



Exemplo de espectro

Etapas de processamento do caldo de cana – Prof. F. Pereira (IQ-UNESP)



Parâmetros instrumentais

Corrente, & tensão

Tempo de medida

R.G. Lima, Mestrado, USP-CENA, 2020

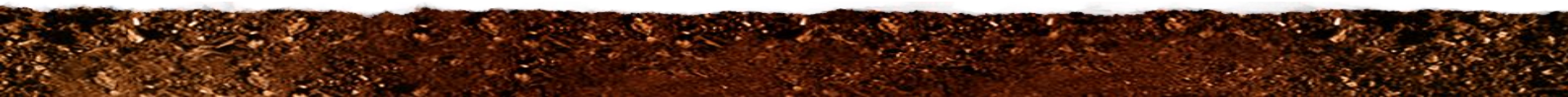
Líquidos ($\mu\text{g L}^{-1}$)

	Limite de detecção ($\mu\text{g L}^{-1}$)						
	Tempo (s)						
Elemento	10	30	90	180	300	600	1000
Ferro	379,0	130,2	65,8	54,4	42,7	30,5	22,3
Gálio	224,9	87,1	49,5	39,0	30,4	20,9	14,7
Selênio	203,8	93,7	43,6	32,3	28,7	19,5	14,4

Suspensão de folhas (mg kg^{-1})

P	K	Ca	Mn	Fe	Cu	Zn	Rb	Sr
856.7	425.6	289.7	10.6	16.5	3.7	5.7	2.7	4.9

Exemplos de aplicação de TXRF



Determinação elemental fluido cerebrospinal

- Volume de amostra empregado: 2 μL
- Tempo de medida: 2000 s

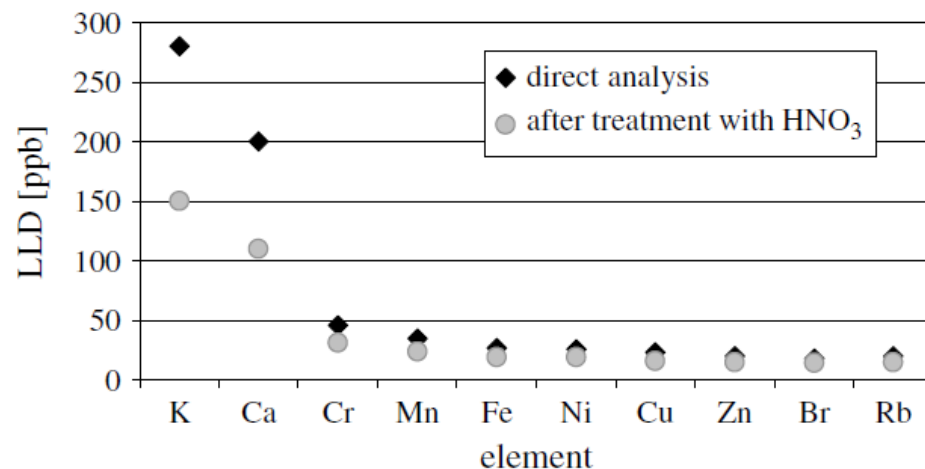
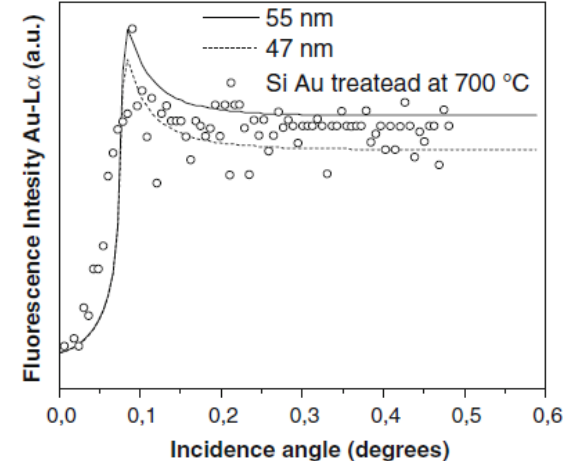
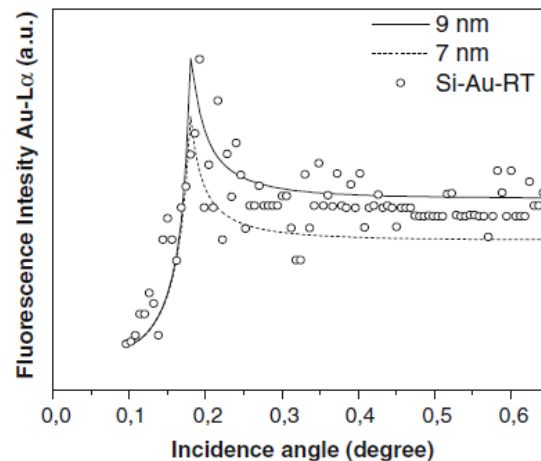
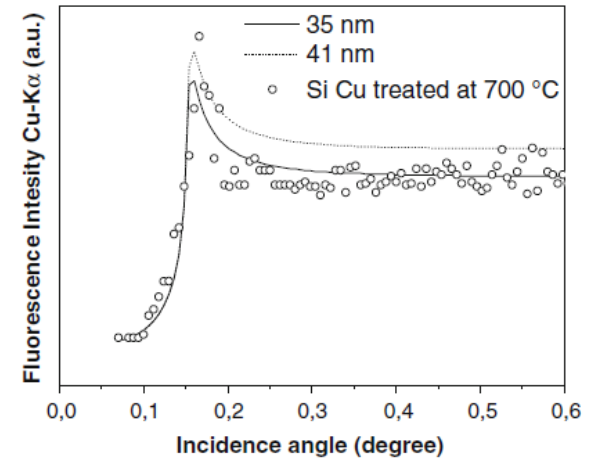
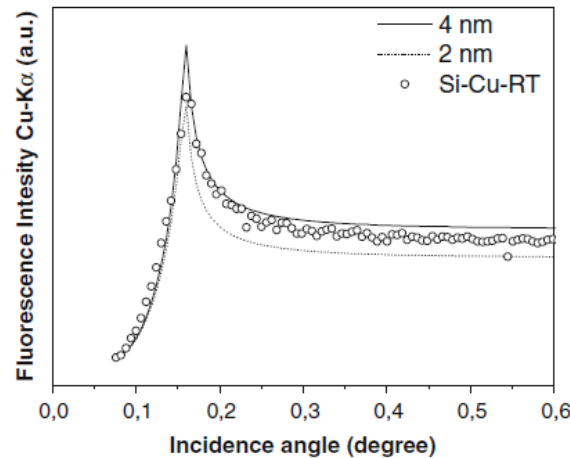


Figure 2. Comparison between the limits of detection for the two methods of the sample preparation.

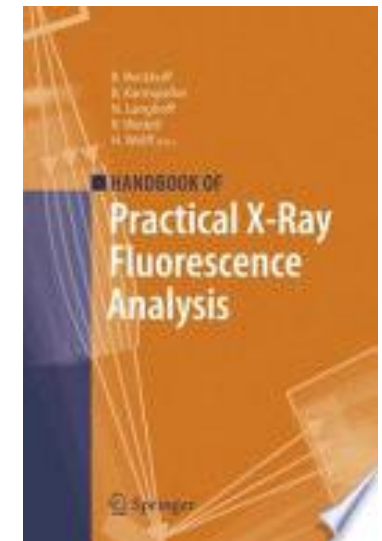
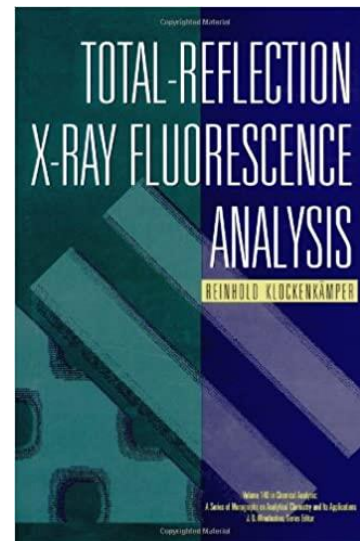


Perfil de implantação de dopantes em wafer de silício

□ A profundidade dos dopante afeta as propriedades fotocatalíticas da superfície



- ❑ Trata-se de uma técnica de fácil preparo de amostra, que demanda poucos consumíveis
- ❑ Ideal quando massa e volume de amostras são fatores limitantes
- ❑ Visto que as amostras são finas, geralmente efeitos de matriz podem ser negligenciados
- ❑ Equipamento com elevado custo de aquisição
- ❑ Limites de detecção equivalentes na ordem dezenas de $\mu\text{g L}^{-1}$ ou $\mu\text{g kg}^{-1}$



Comparação entre técnicas

μ -XRF

- ✓ Amostras heterogêneas
- ✓ Preparo simples ou desnecessário
- ✓ Processos dinâmicos com resolução lateral
- ✓ LOD *ca.* mg a g kg⁻¹

TXRF

- ✓ Amostras homogêneas
- ✓ Preparo é simples
- ✓ Restrição de volume/massa em baixa concentração
- ✓ LOD *ca.* μ g a mg kg⁻¹