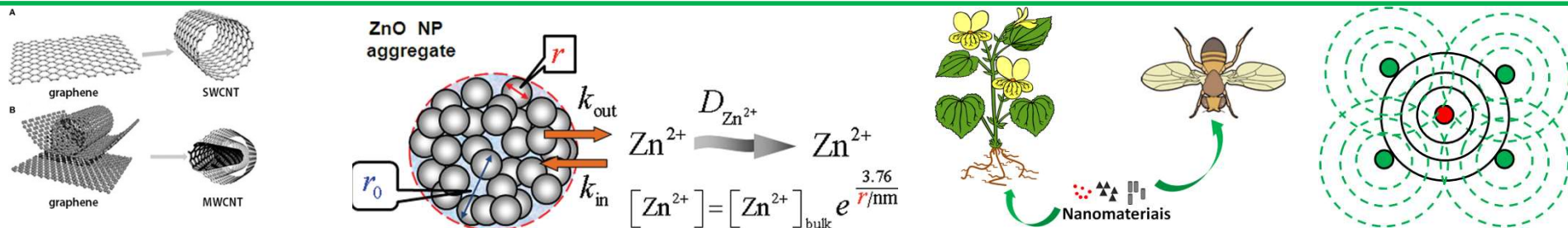




X-ray Fluorescence Spectrometry

Prof. Hudson W.P. Carvalho



Main Features of XRF

- ❑ Fundamentals of XRF
- ❑ Variants of XRF
- ❑ Quantification strategies
- ❑ Sample preparation
- ❑ Examples of application

Main Features of XRF

- ❑ Qualitative analysis (from Na)

- ❑ Quantitative analysis

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

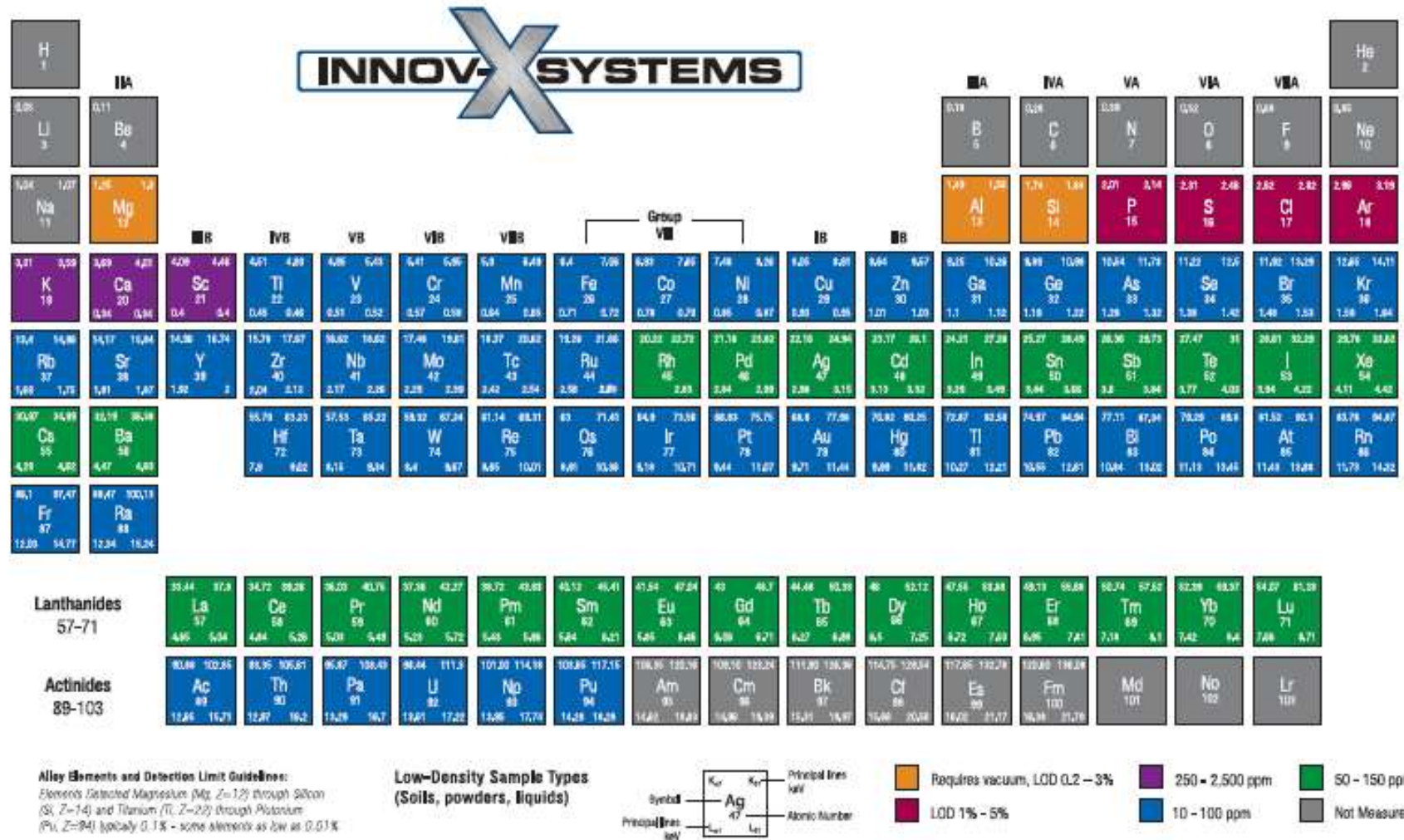
- ❑ From Na to U (usually)

- ❑ Non-Destructive

- ❑ Minimum sample preparation is required

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

Limits of detection in XRF



Lab Equipments for XRF

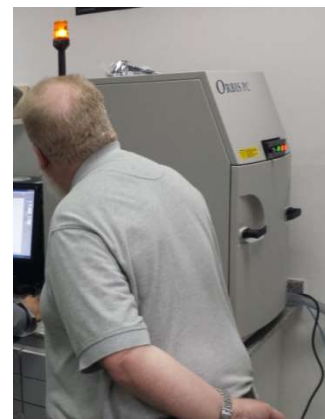
Handheld XRF \$ 50 K



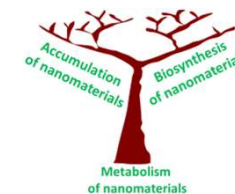
EDXRF \$ 60 K



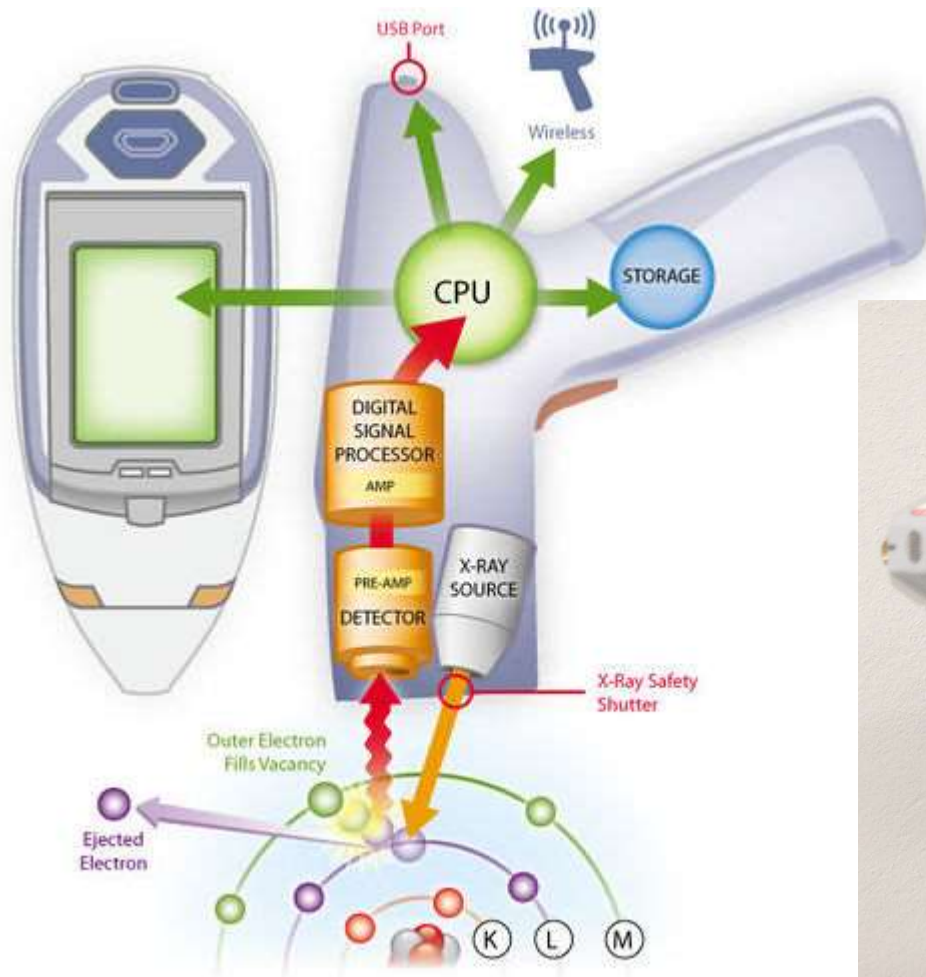
Total Reflection XRF \$ 90 K



\$ 180 K
Micro-XRF



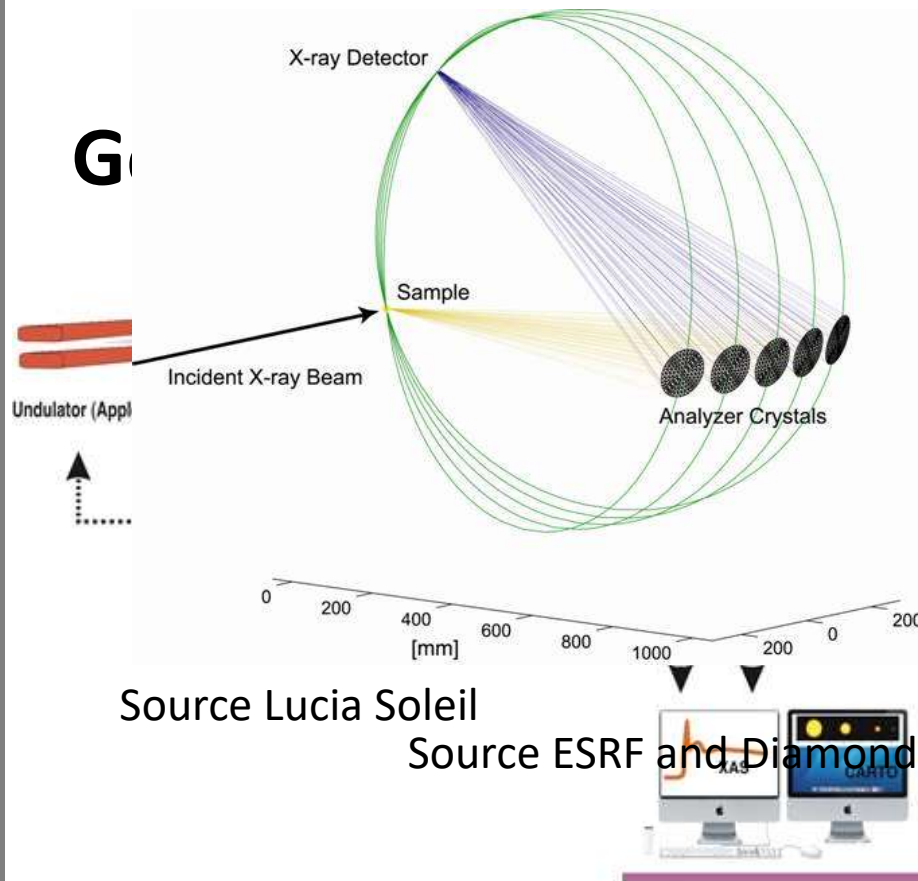
Fluorescência de raios X



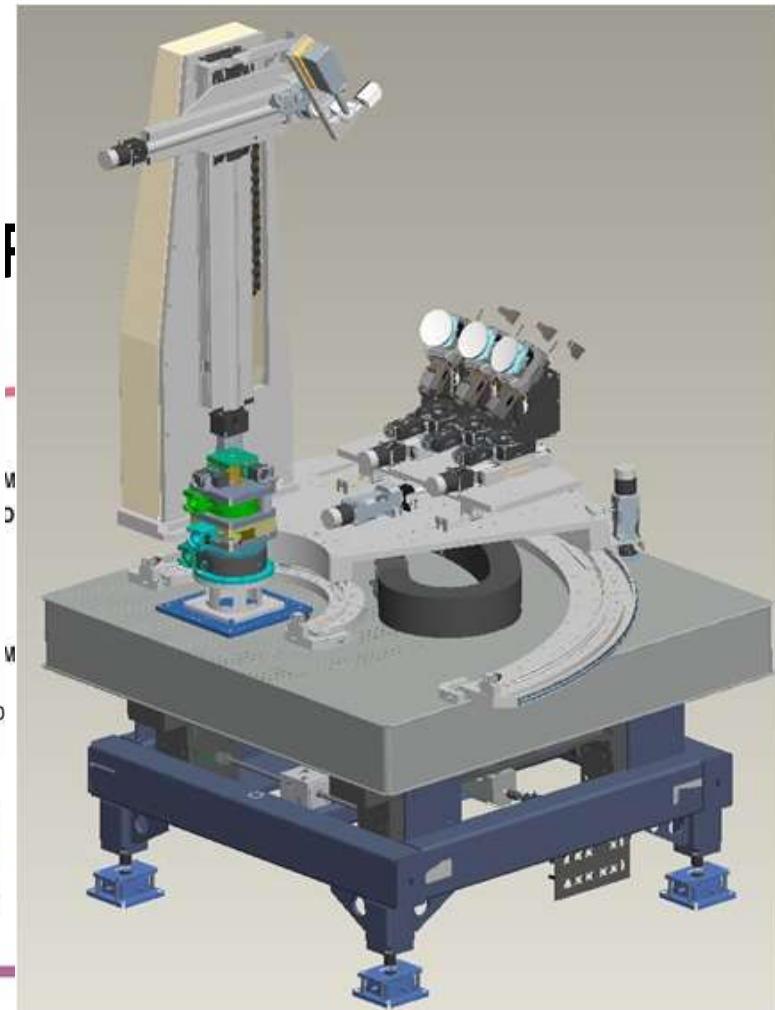
[https://openei.org/wiki/Hand-held_X-Ray_Fluorescence_\(XRF\)](https://openei.org/wiki/Hand-held_X-Ray_Fluorescence_(XRF))

Large Facilities for XRF

XRF beamlines in synchrotron sources



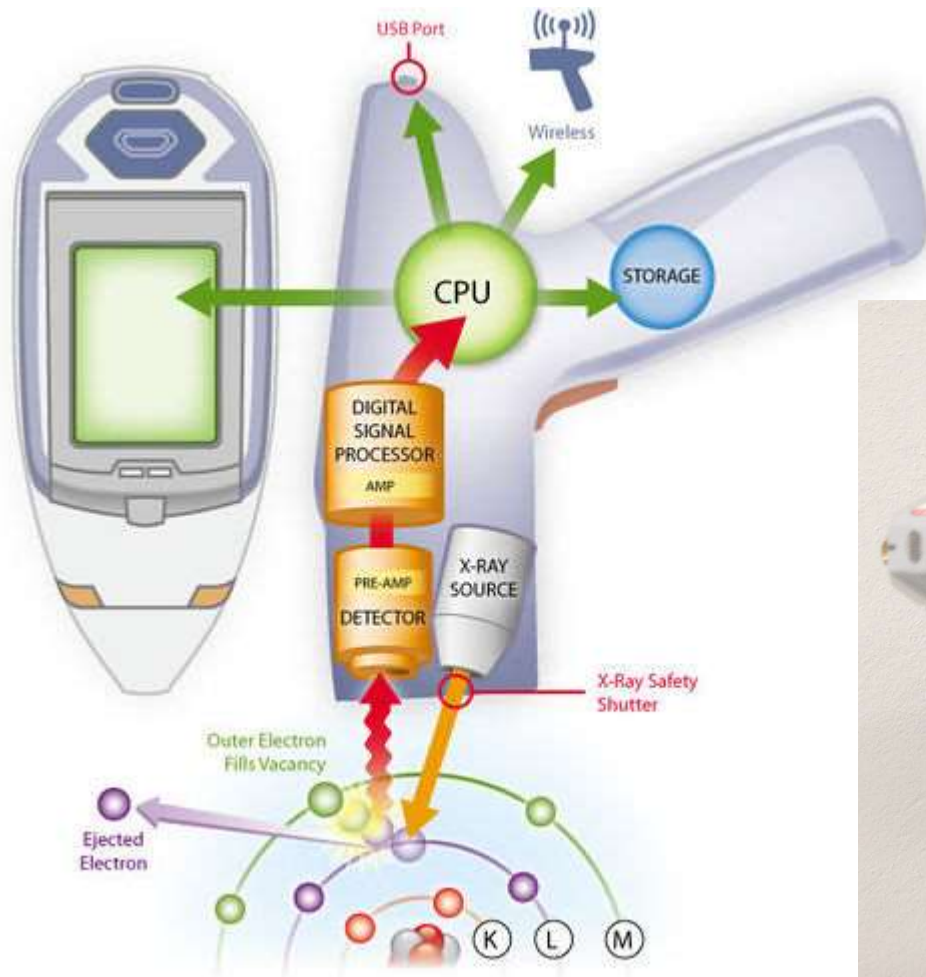
Crystal analyzer for High Energy Resolution XRF



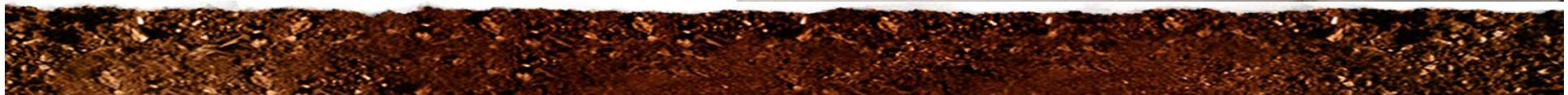
Yield
mission
tor

**What is the common point
between all these XRF
equipments?**

Fluorescência de raios X



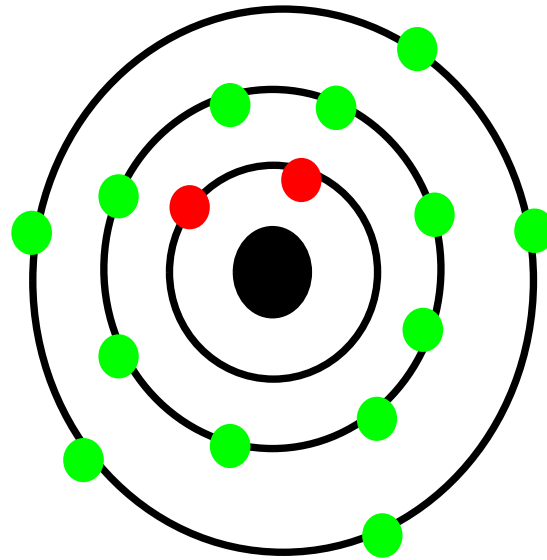
[https://openei.org/wiki/Hand-held_X-Ray_Fluorescence_\(XRF\)](https://openei.org/wiki/Hand-held_X-Ray_Fluorescence_(XRF))



Fluorescência de raios X

Fonte de raios X

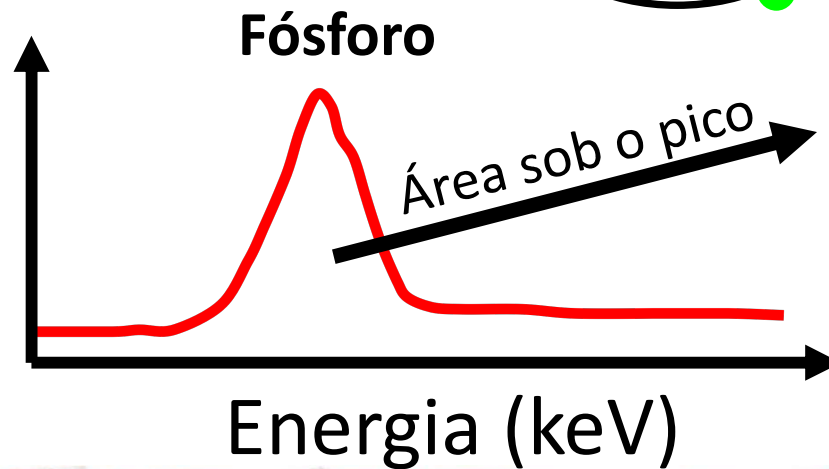
Átomo da Amostra



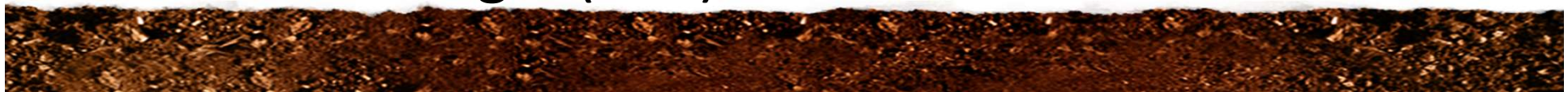
Detector de raios X característicos

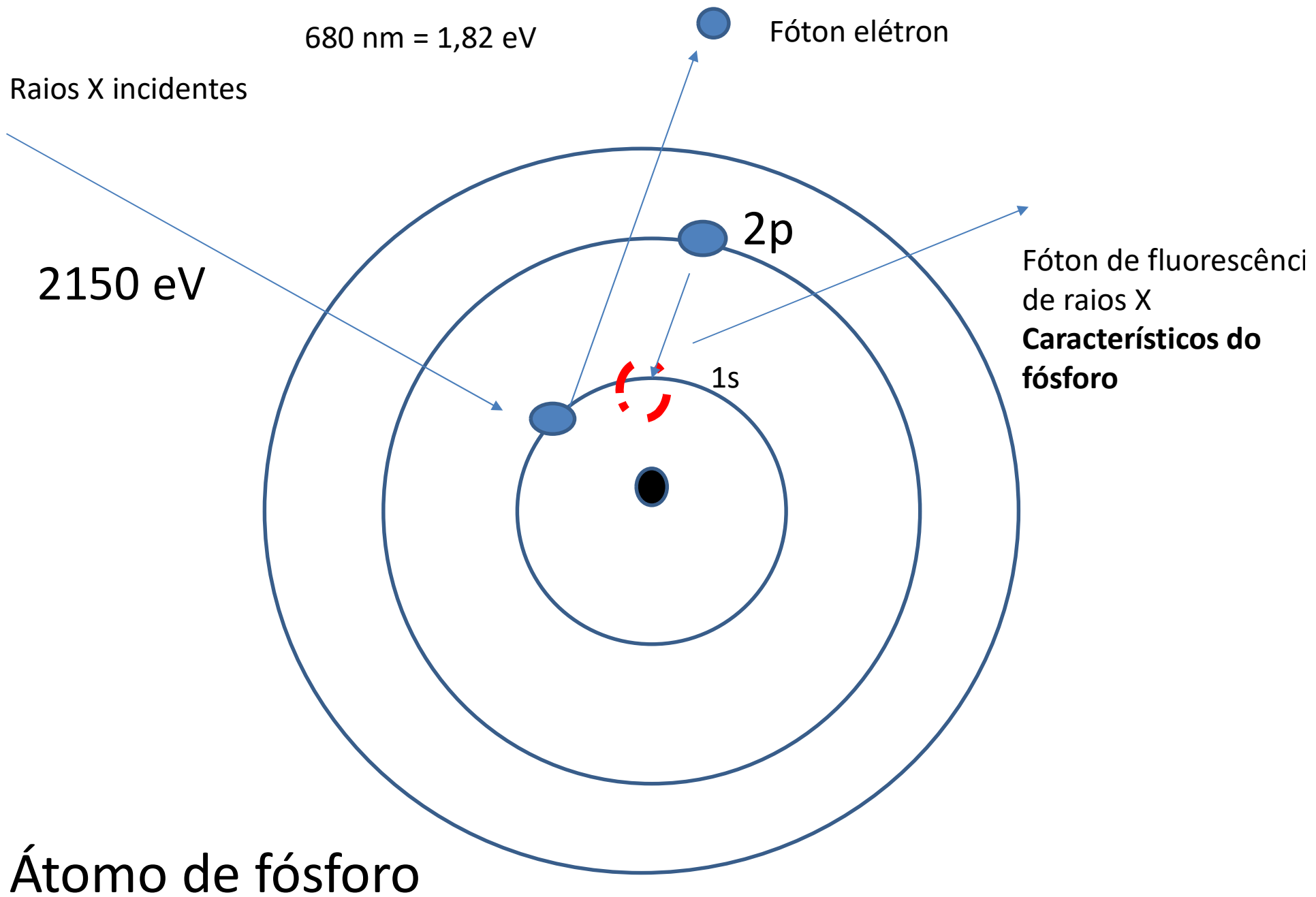
☐ O detector gera um espectro

Contagens (cps)



1 g kg⁻¹
Concentração





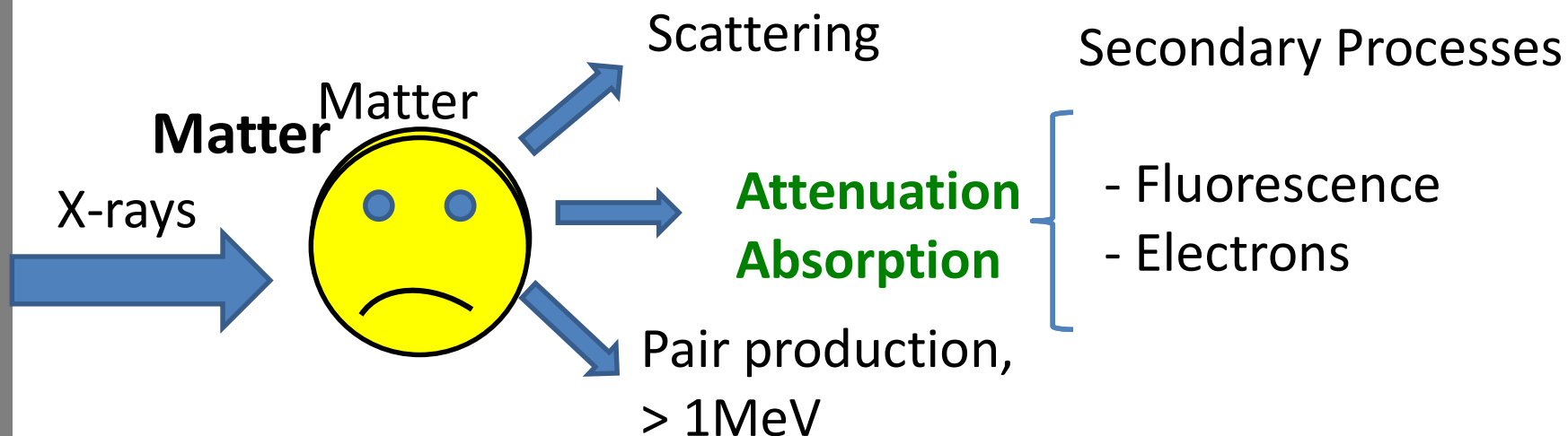
Do Laboratório para o Campo



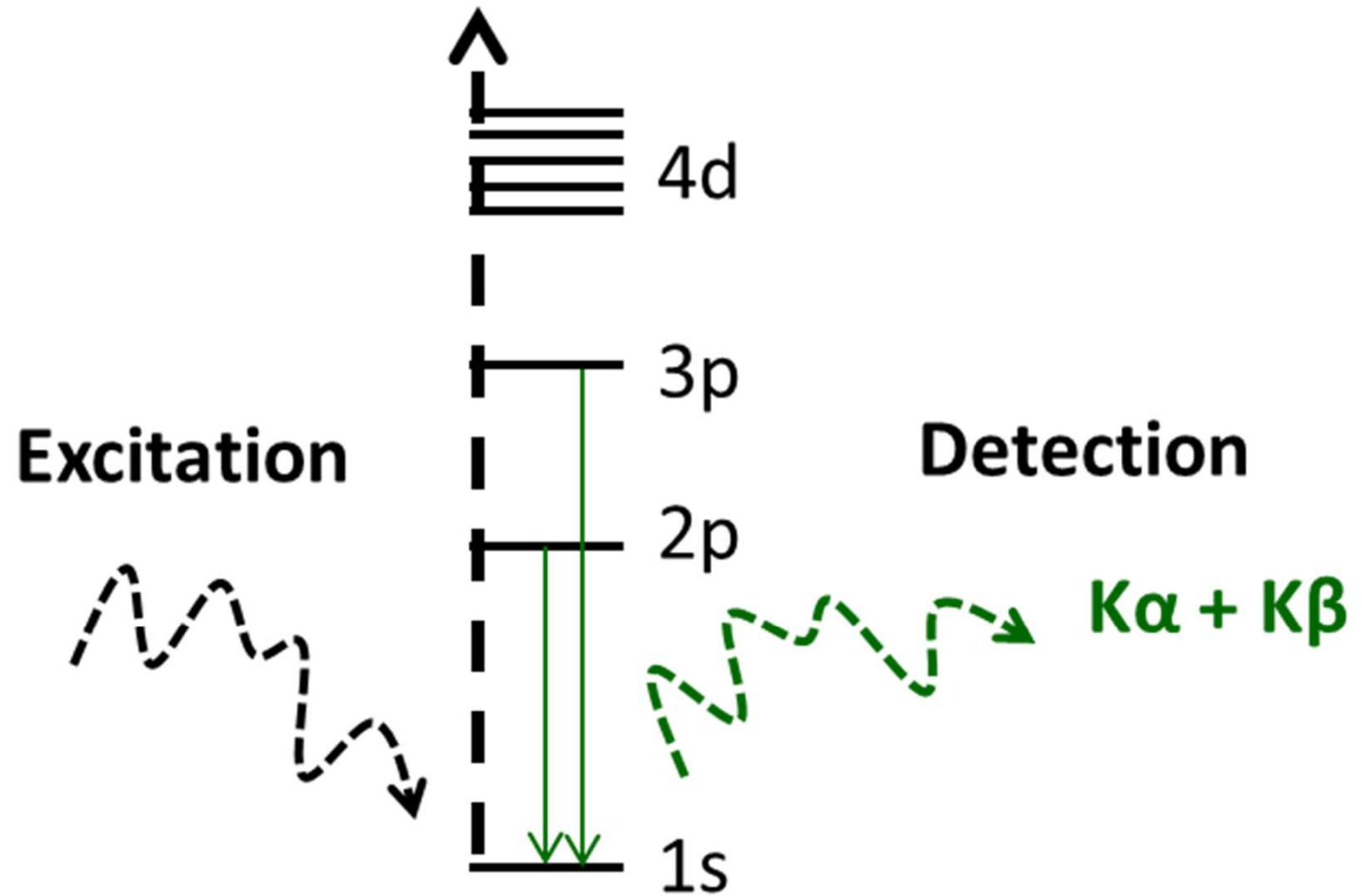
Ferti-Móvel

Principles of XRF - radiation and matter

□ How does matter and light interact?

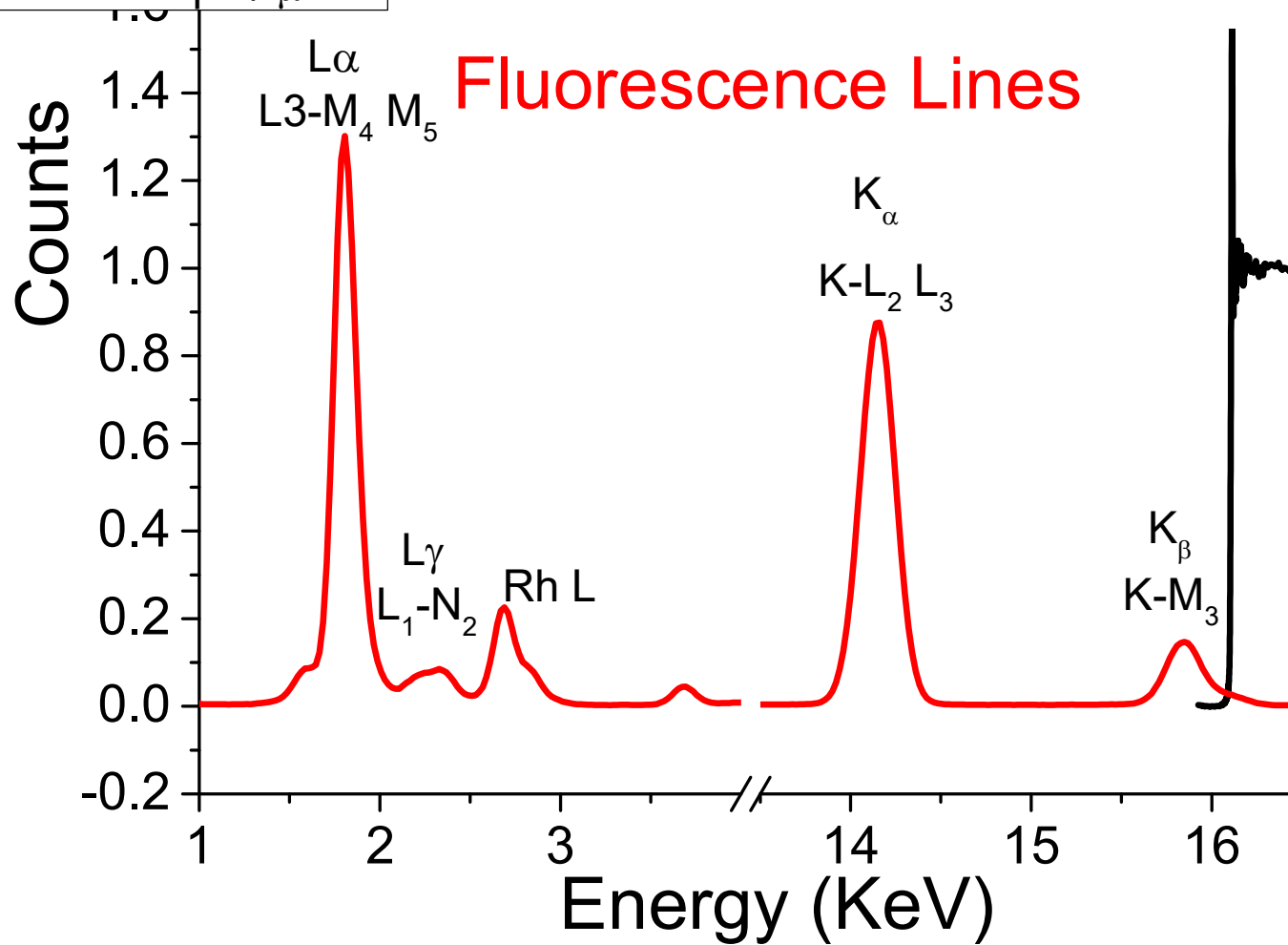


What does happen after absorption?

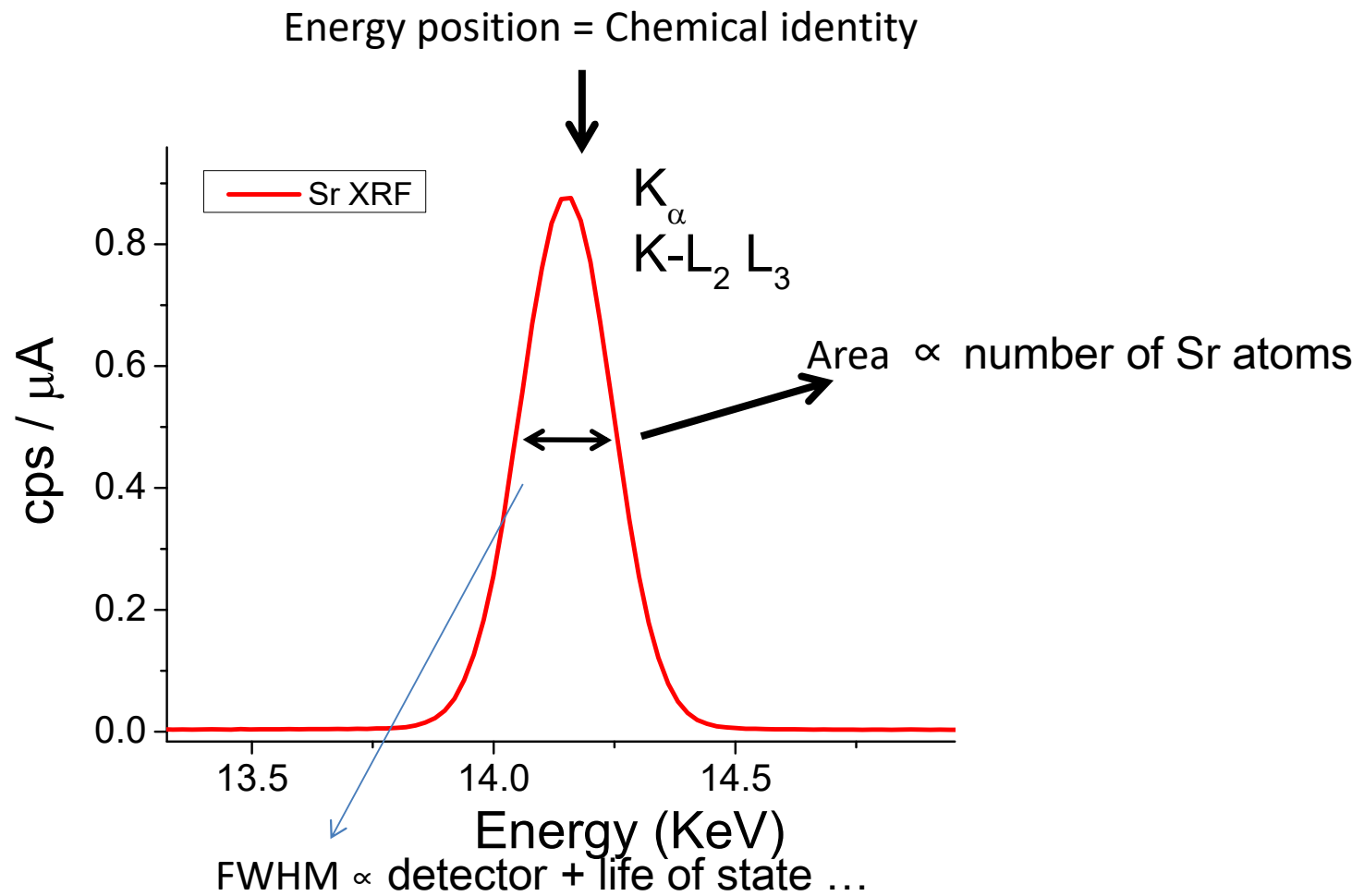


First XAS, then XRF

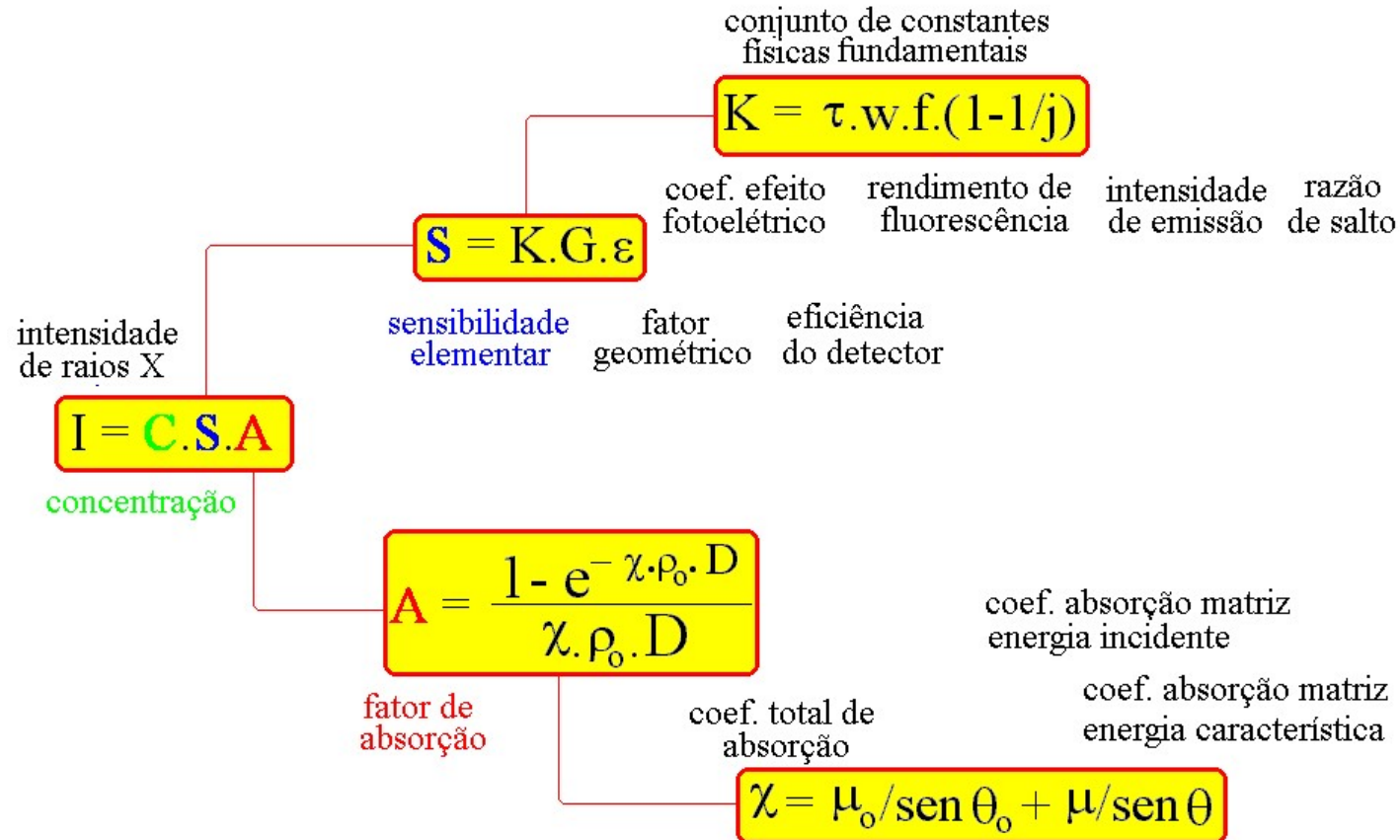
— XAS Norm $\mu x(E)$
 — XRF cps / μA



An XRF peak



Quantitative XRF

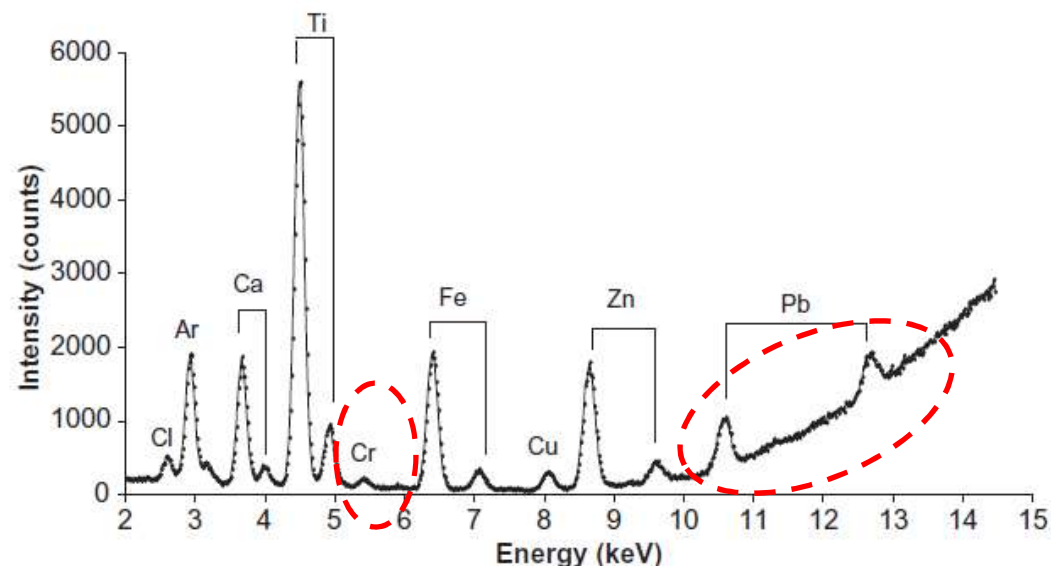


Quantification Strategies

- Parâmetros fundamentais – a quantificação é feita sem curva analítica de calibração (*ab initio*)
- Curvas de calibração com padrões cuja composição é similar a composição da amostra**
- Calibração com método de referência
- Calibração por adição de padrão – adicionar concentrações conhecidas do analito na amostra e com isso determinar a sensibilidade

Quali and Quanti XRF

□ The inorganic composition of plastic garbage bags



X-ray spectrum of a garbage bag (sample no. 9). The acquisition time was 500 s.

□ Lots of Cr and Pb were found

International Journal of Environmental Analytical Chemistry

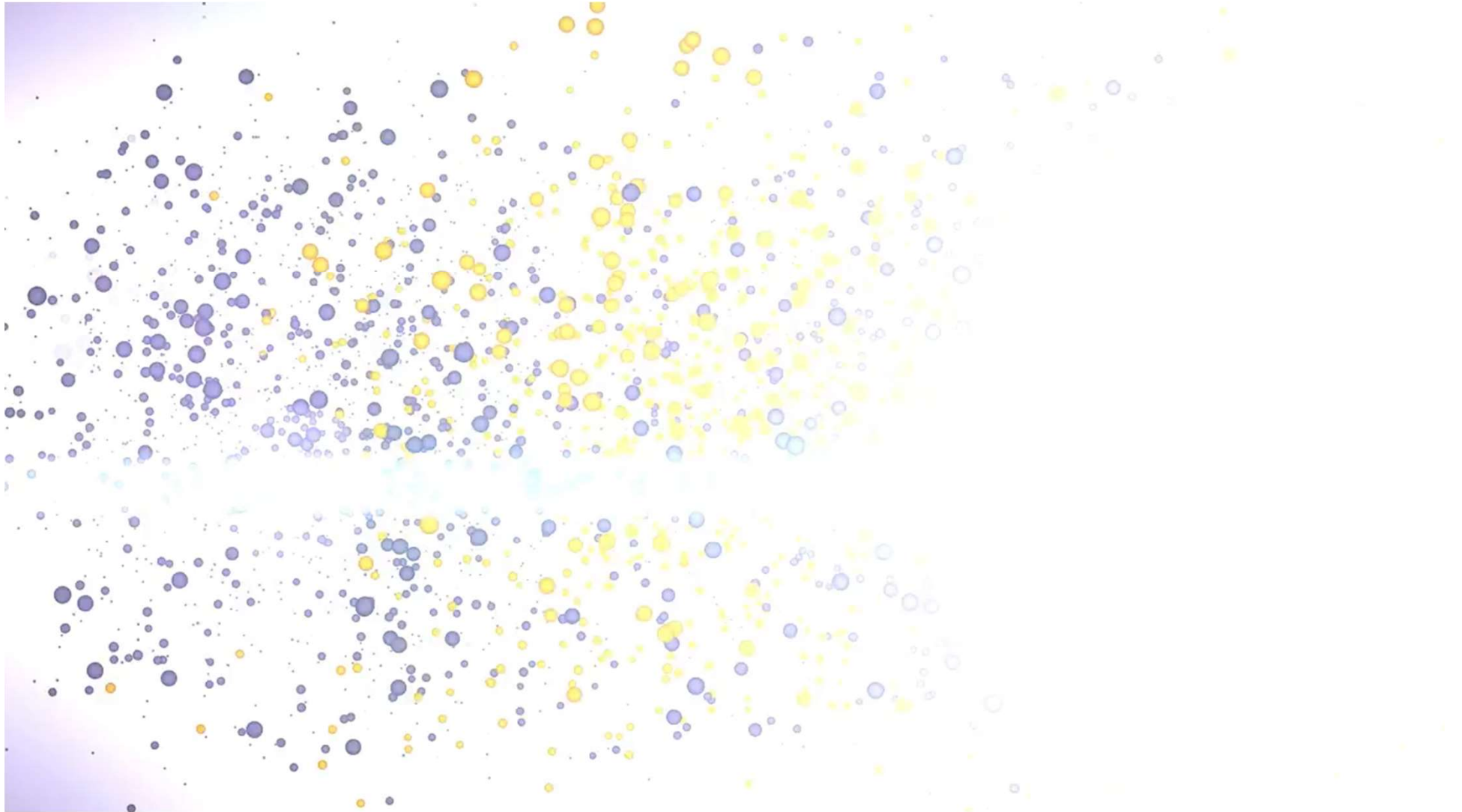
Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/geac20>

Multielemental evaluation of garbage bags by EDXRF

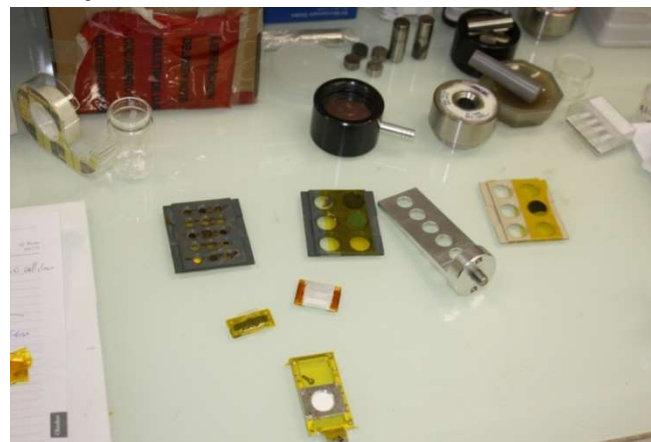
Eduardo de Almeida^a, Alexandre D. M. Cavagis^b, Amauri Antonio Menegário^c & Virgílio Franco Nascimento Filho^a

Sample preparation



Sample preparation

- From simple pellets, like those for IR




- Cups for powders or liquids



http://media.noria.com/sites/archive_images/Backup_200405_XRF-Fig4.jpg

Sample preparation

☐ Direct analysis by XRF?

liquids	rocks, minerals, ores, ceramics, ...	metals	glass, polymers	small pieces, chips, wires
				
				
				
				
				
				
10 s	10 s			
10 s	10 s			
	2 min			
	10 min			
		1 min		
			2 min	
				5 s

Preparation of Liquid Samples

☐ Direct analysis

0-35-130
0-35-135
0-35-160
0-35-240
0-35-260



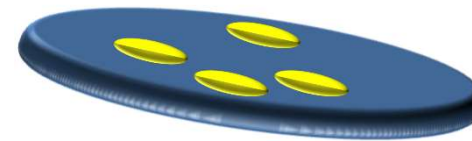
35 mm Cups

Catalog No.	Sample Cup Type	Film Type
PA-200-35-130	SC-3335	Mylar® 3.0μ (0.12 mil)
PA-220-35-135	SC-3335	Mylar® 3.5μ (0.14 mil)
PA-240-35-160	SC-3335	Mylar® 6.0μ (0.24 mil)
PA-260-35-240	SC-3335	Polypropylene 4.0μ (0.16mil)
PA-280-35-260	SC-3335	Polypropylene 6.0μ (0.24 mil)

☐ Dried residue



Homogeneous



Non-Homogeneous

☐ How to correct this issue?

Preparation of Metals

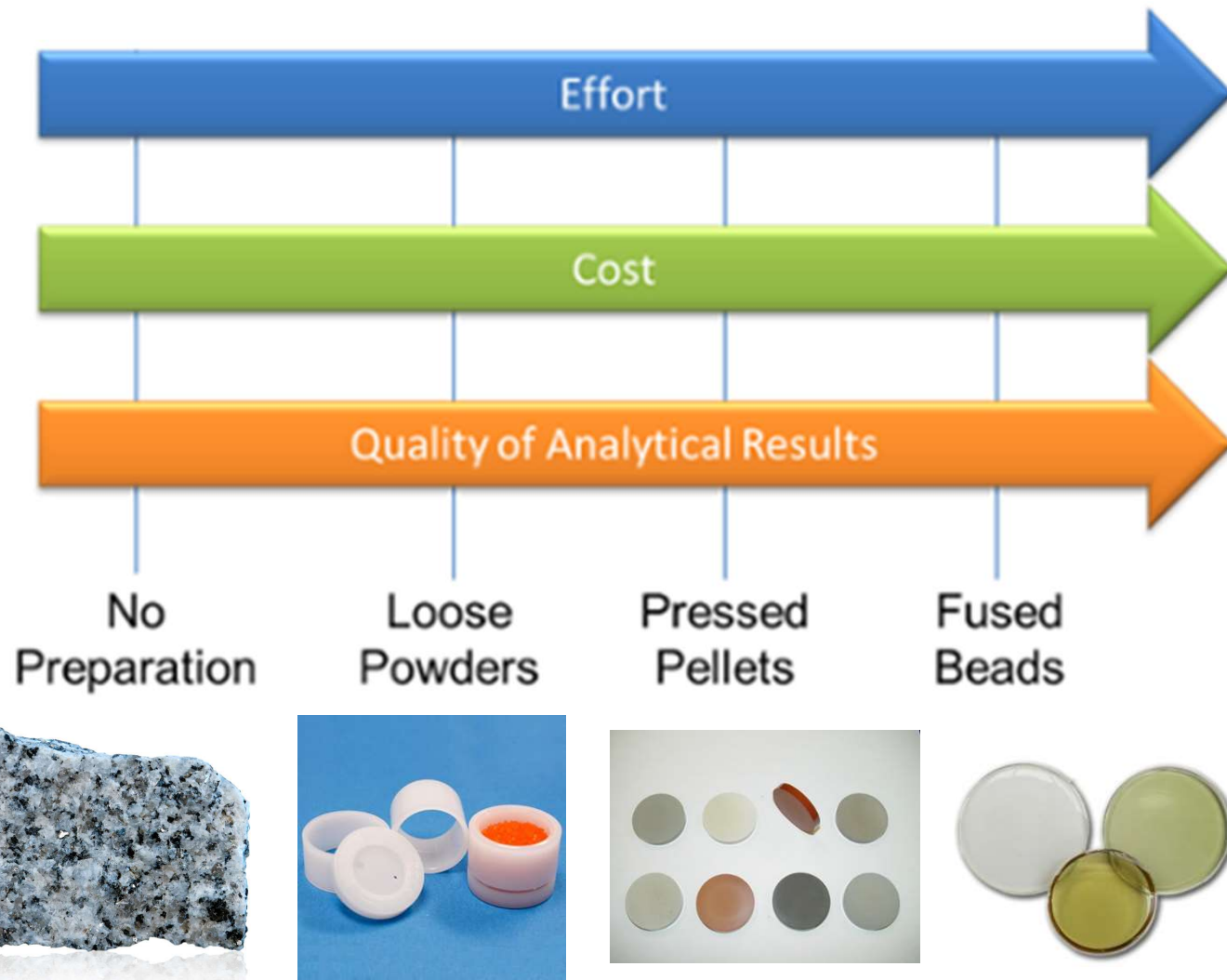
- Polishing the surface



Machined and polished sample

http://www.shimadzu.de/sites/default/files/sites/files/edx70008000_37.jpg

Cost vs effort for solids



https://cdn.nexternal.com/tsp/images/40-1000_l.jpg



<http://labauto.flsmidth.com/blog/the-5-most-common-ways-to-prepare-samples-for-xrf-analysis>



Sources of Error in XRF

The Golden Rule for Accuracy with XRF

Since the highest accuracy in XRF is achieved by comparing unknowns with standards, the standards and unknowns must be as similar as possible in mineralogy, particle size, particle homogeneity and matrix characteristics.

Bruker AXS

Limits of detection in XRF

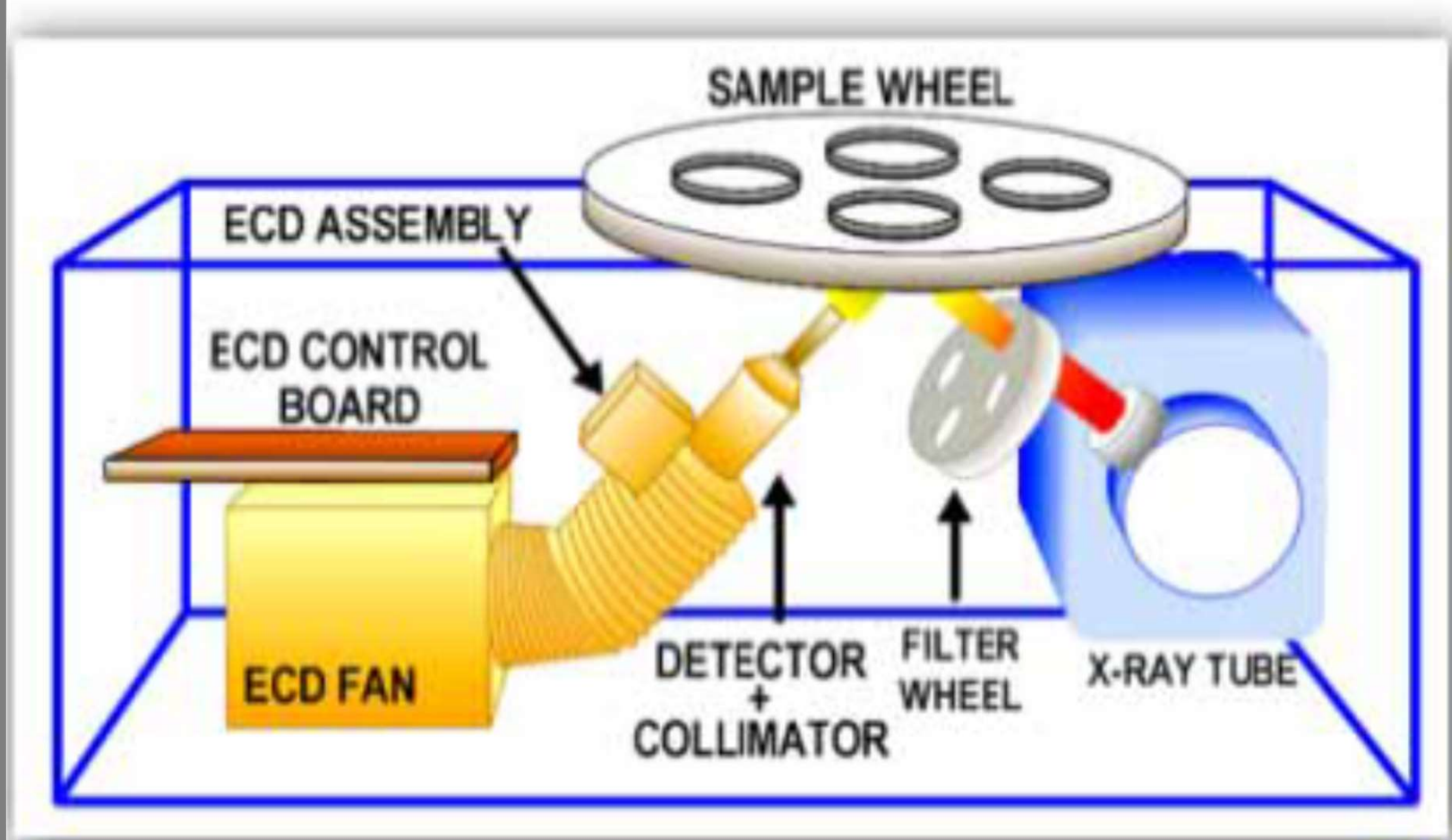
- For measurements in optimal conditions

In ppm (mg L ⁻¹)	EDXRF	WDXRF	μ-XRF	TXRF
LOD Cu Kα	10	0.5	5	0.001
LOD Hg Lα	10	1.2	5	0.008

Which one should you chose?

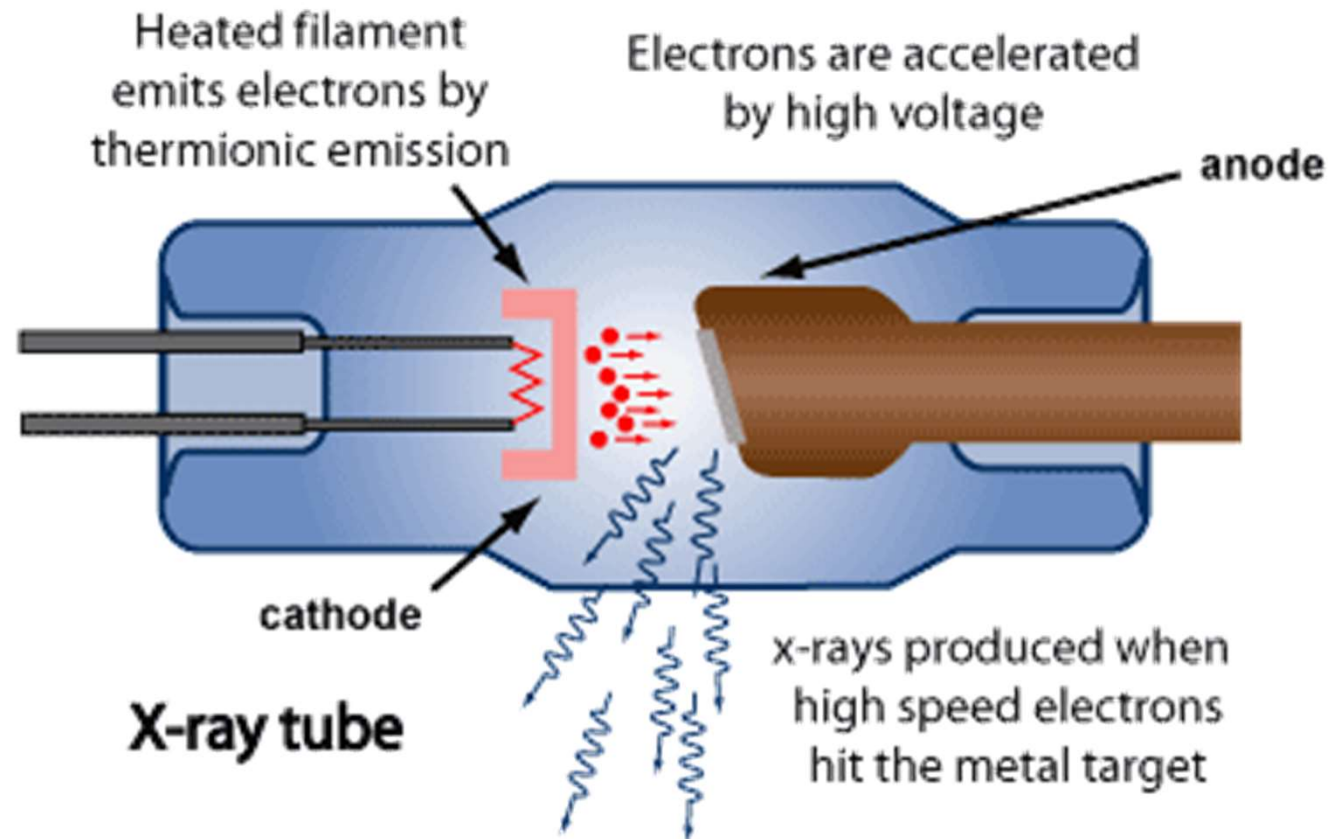
- EDXRF: should be the first choice
- WDXRF: When you already know the composition
- μ-XRF: Only for mapping
- TXRF: Ideal for liquids or fine powders

EDXRF



X-ray Sources

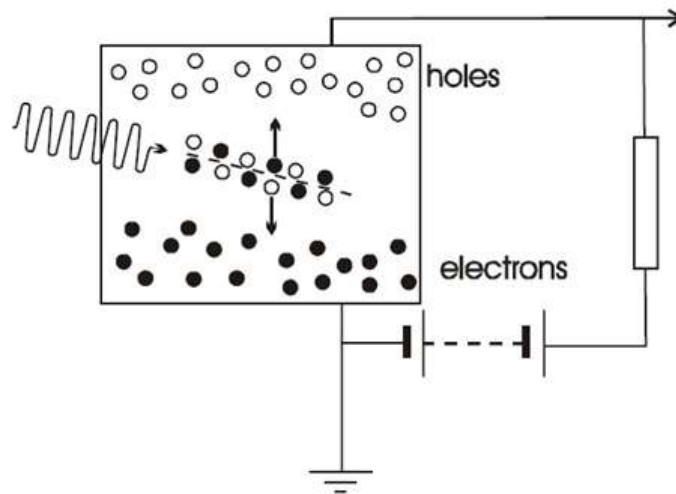
□ Components of an X-ray tube



<http://www.arpana.gov.au/images/basics/xraytube.png>

X-ray Detectors

❑ Semiconductors



<http://nsspi.tamu.edu/media/879755/image1.jpg>

❑ Multichannel Analyzers



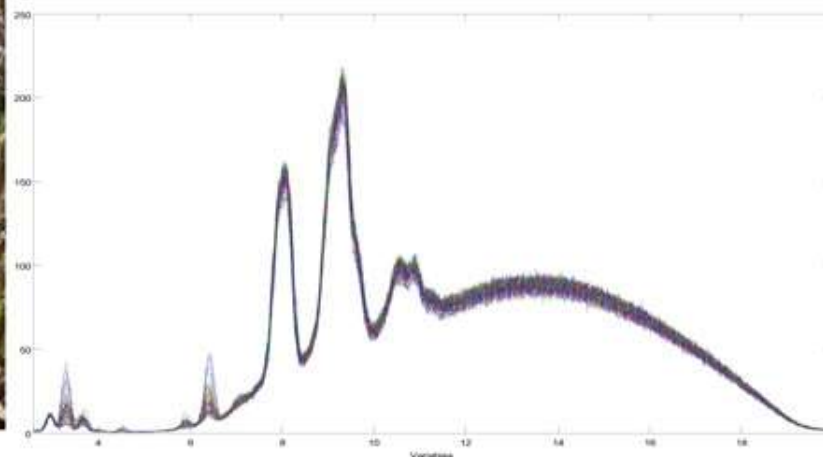
Revisão da aula

- XRF ou FRX é uma técnica analítica que permite a análise direta de sólidos
- Ele faz análises qualitativas e quantitativas
- O preparo de amostras é simples, geralmente moagem ou simplesmente deposição de líquido em um substrato
- O fenômeno de XRF decorre da relaxação de um “core hole” ou buraco num orbital de camada profunda

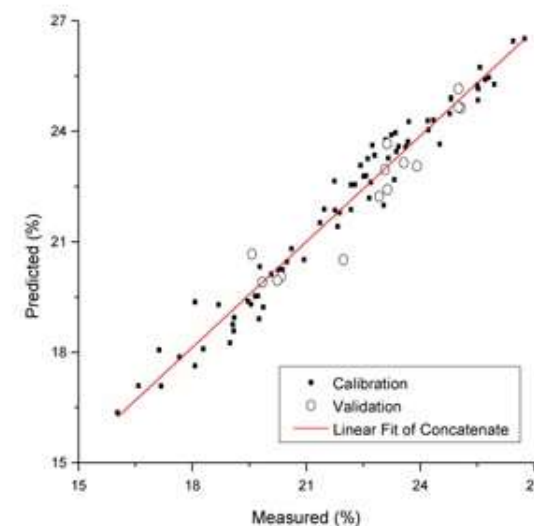
EDXRF Examples

Valoração de produto

❑ 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^{||}

[†]Universidade Estadual do Centro Oeste, Rua Presidente 6 Zacarias, 875,85015-430, Guarapuava, PR, Brazil

[‡]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



Valoração de produto

- ❑ 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

