Compositional analysis of archaeological ceramics by Handheld XRF

Examples of pottery sherds showing the complexity of target ceramic materials

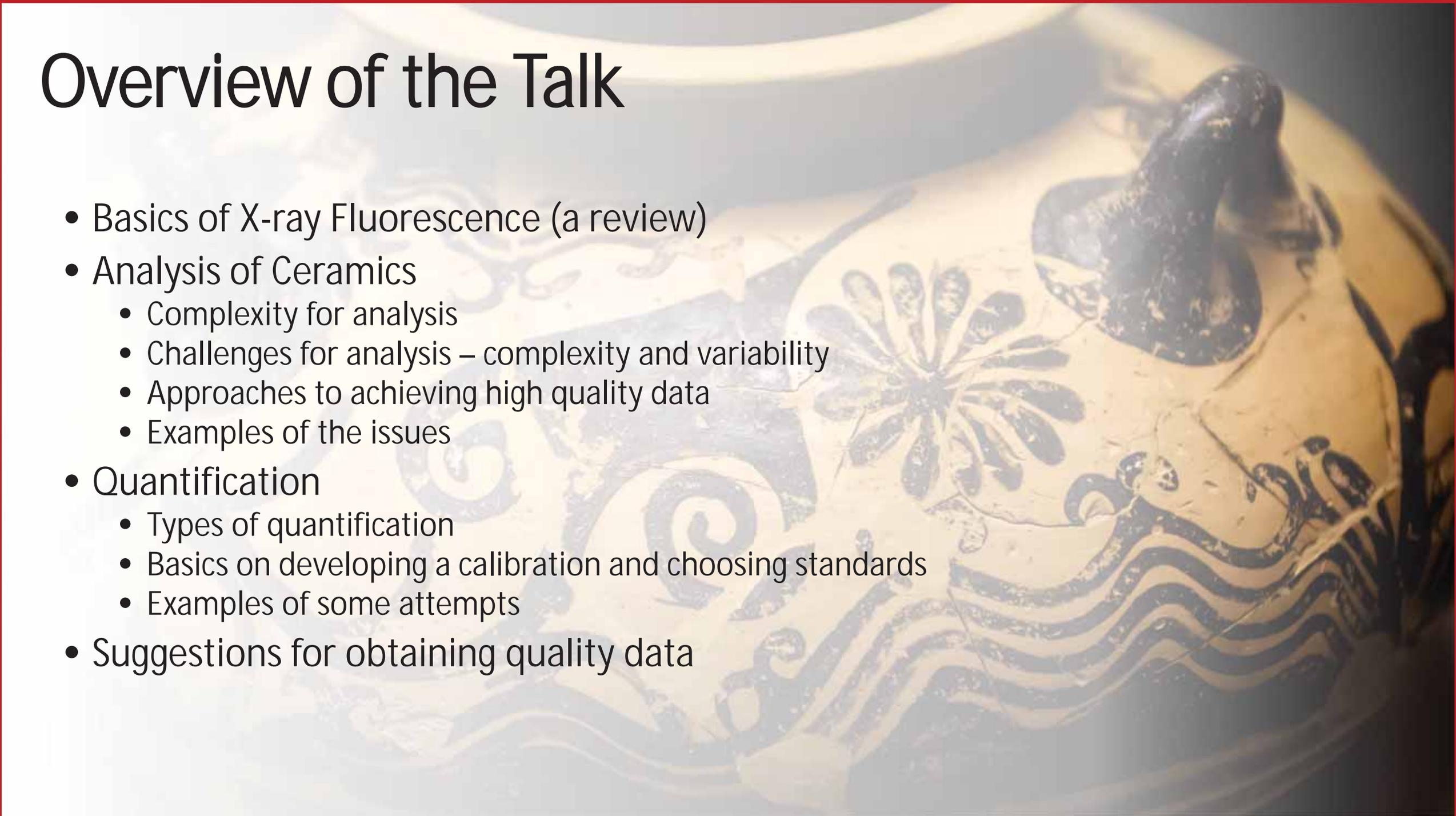Archaeological ceramics in situ

Prof. Aaron Shugar
Art Conservation Department,
SUNY Buffalo State College

Dr. Nigel Kelly
Senior Market Application Scientist,
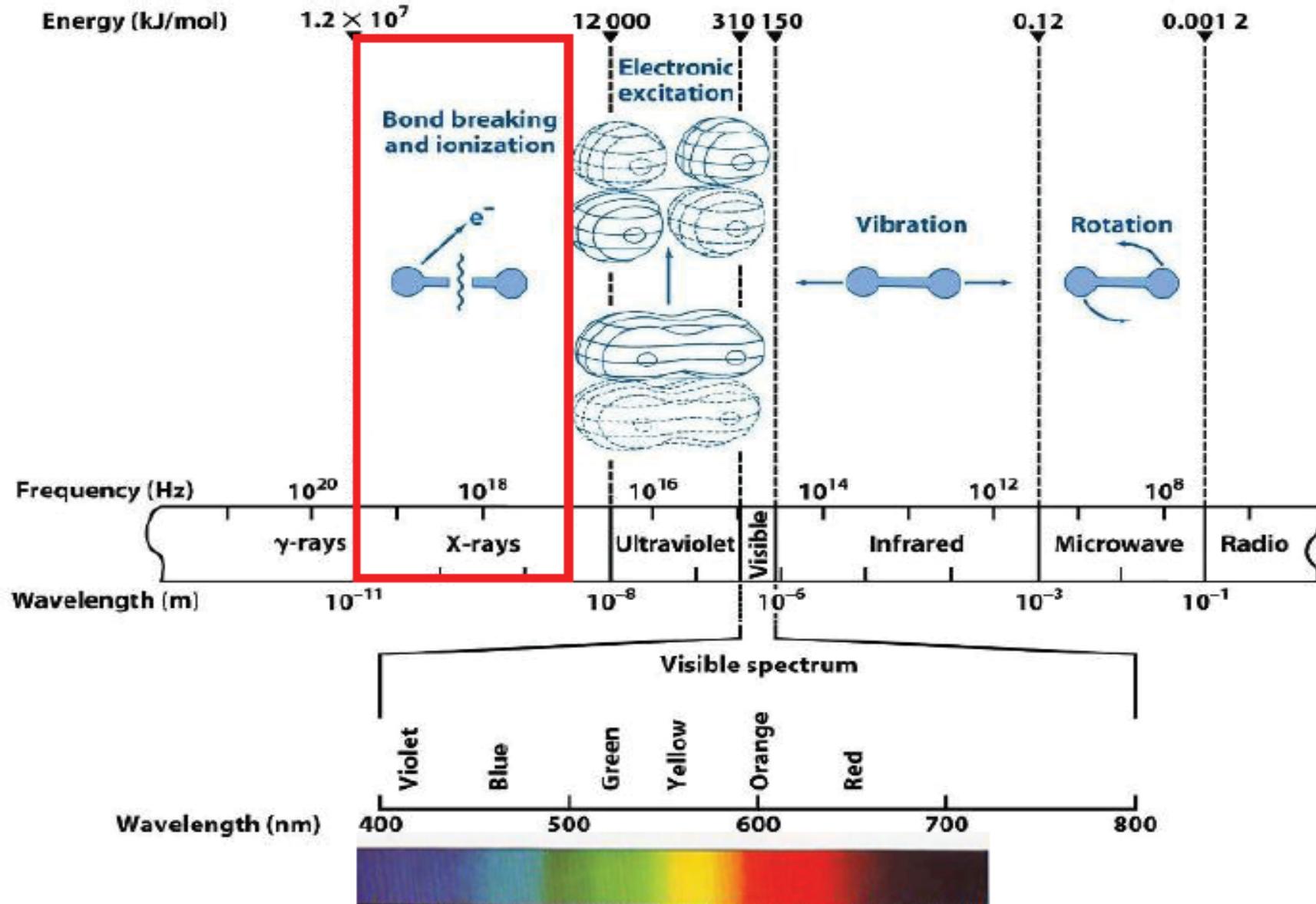Bruker Nano Analytics

Overview of the Talk

- Basics of X-ray Fluorescence (a review)
- Analysis of Ceramics
  - Complexity for analysis
  - Challenges for analysis – complexity and variability
  - Approaches to achieving high quality data
  - Examples of the issues
- Quantification
  - Types of quantification
  - Basics on developing a calibration and choosing standards
  - Examples of some attempts
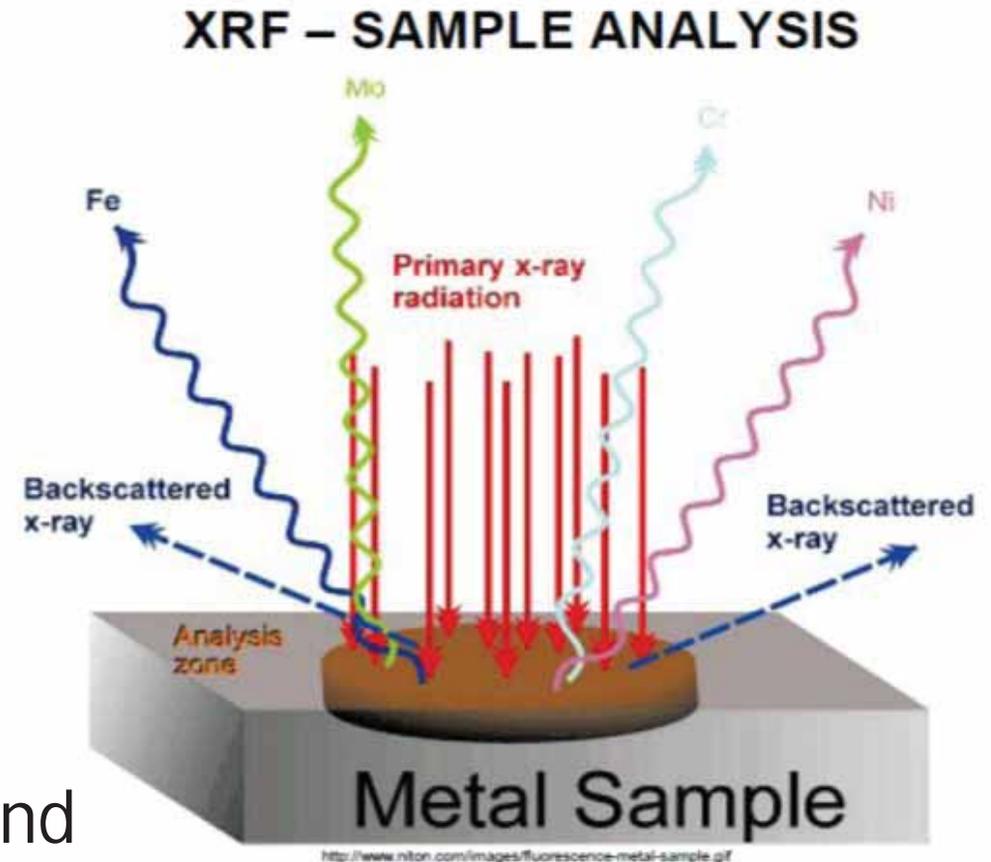- Suggestions for obtaining quality data

THE ELECTROMAGNETIC SPECTRUM
How does light affect molecules and atoms?

Energy (kJ/mol): 1.2×10^7 12 000   310 150   0.12   0.001 2

Bond breaking and ionization

Electronic excitation

Vibration

Rotation

e^-

Frequency (Hz): 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^8

γ-rays   X-rays   Ultraviolet   Visible   Infrared   Microwave   Radio

Wavelength (m): 10^{-11} 10^{-8} 10^{-6} 10^{-3} 10^{-1}

Visible spectrum

Violet   Blue   Green   Yellow   Orange   Red

Wavelength (nm): 400   500   600   700   800

D.C. Harris, Quantitative Chemical Analysis, 7th Ed., Freeman, NY, 2007.
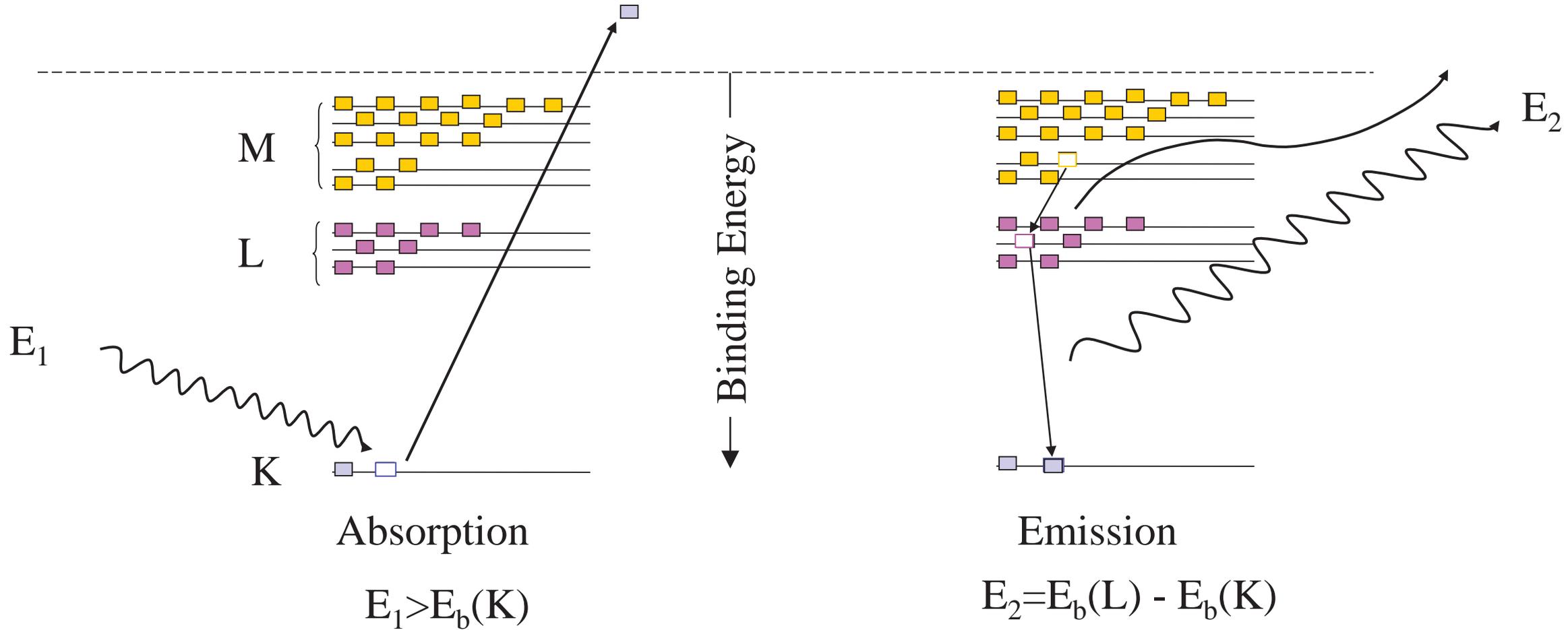
The X ray Reactions in the Sample

- **Compton**: inelastic scattering
- **Raleigh**: elastic scattering
- **Bragg**: coherent scattering
- **Electron ejection**: X ray fluorescence
- **Inter element effects**:
  - Secondary fluorescence
  - Sample absorption
  - Density effects
- Reaction probability as a function of incoming x ray energy
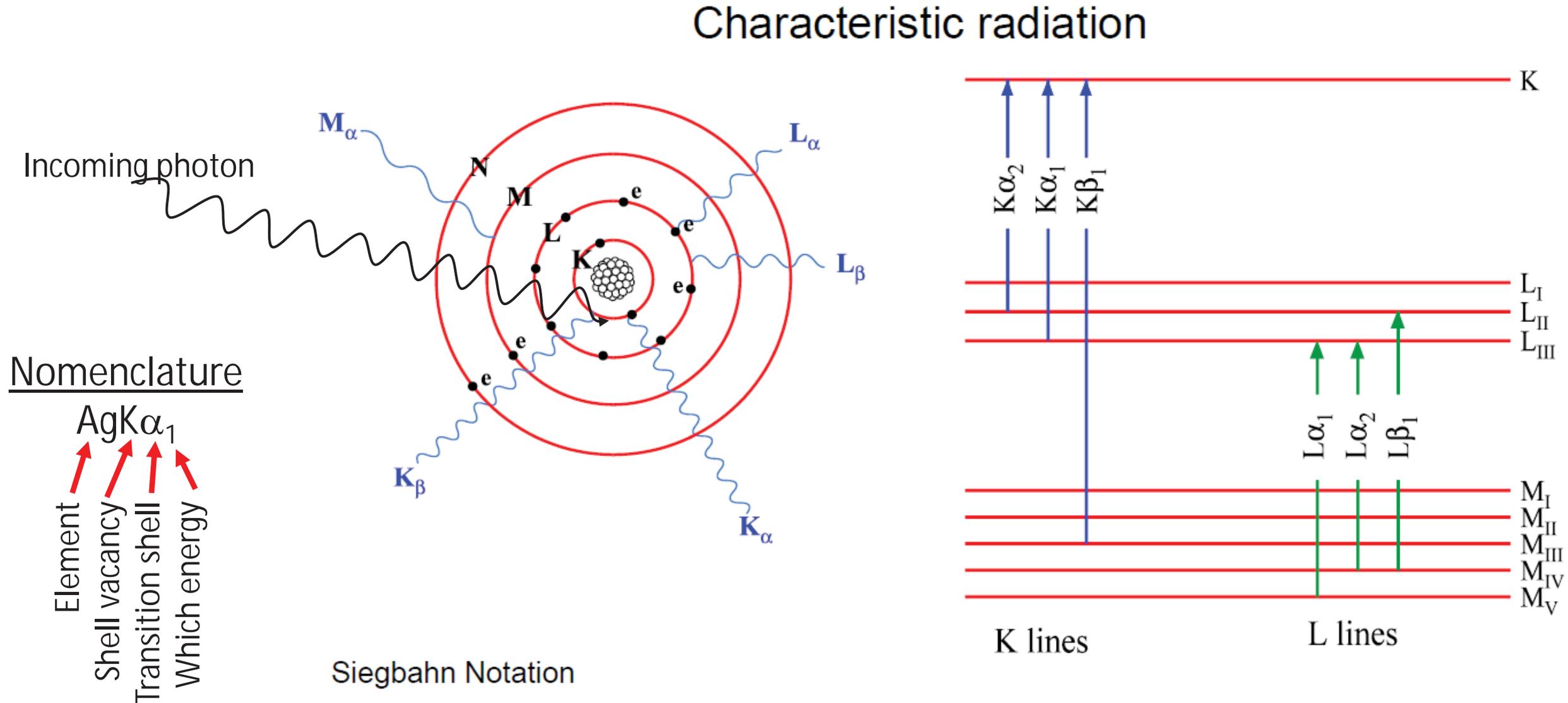- **Attenuation** as function of x ray energy and material type

XRF – SAMPLE ANALYSIS

Mo

Fe

Cr

Ni

Primary x-ray radiation

Backscattered x-ray

Backscattered x-ray

Analysis zone

Metal Sample

http://www.niton.com/images/fluorescence-metal-sample.gif

- Since the *electronic energy levels for each element are different*, the energy of X-ray fluorescence peak can be correlated to a specific element
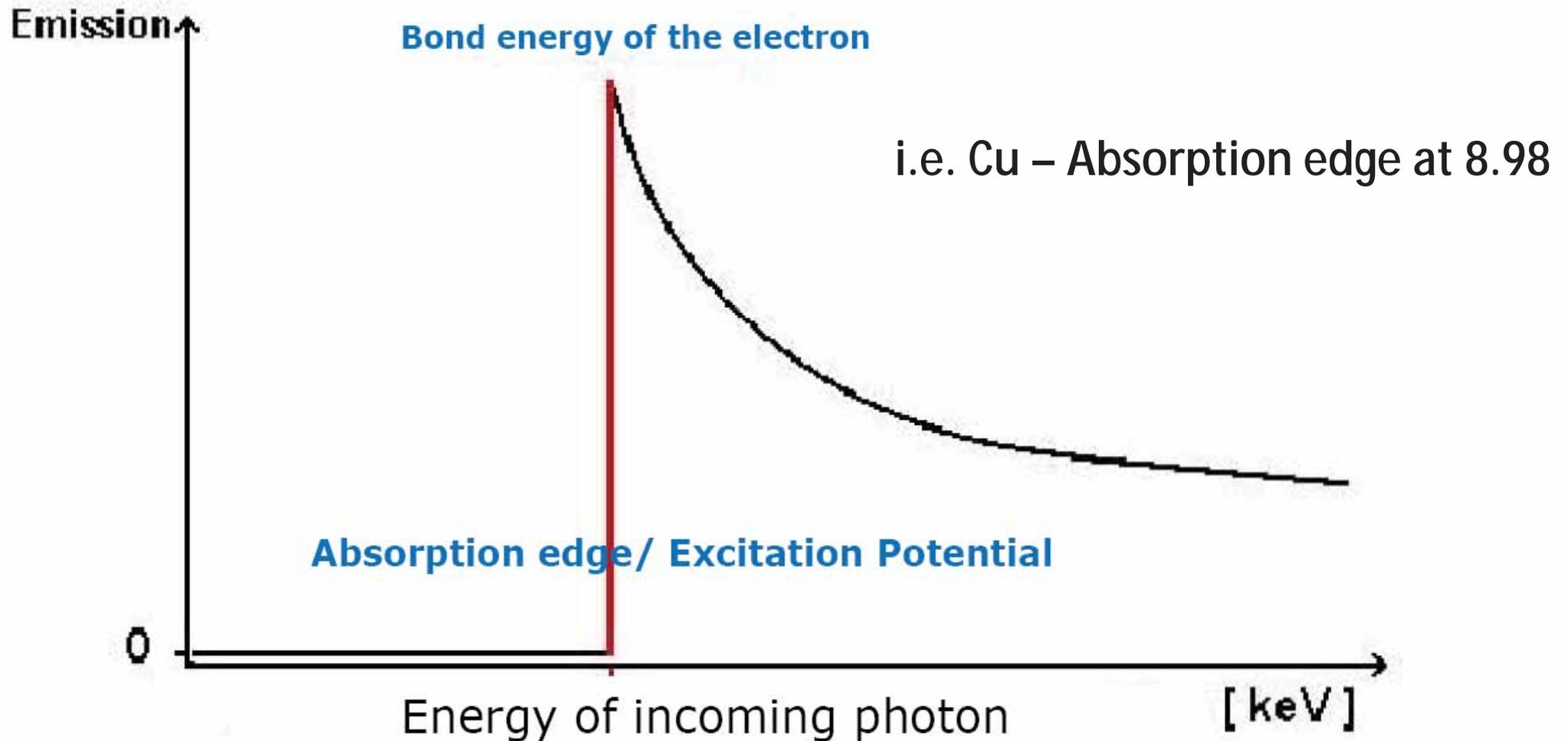
# Electrons, the Photoelectric Effect and Fluorescence

M

L

E_1

K

Binding Energy

Absorption

$E_1 > E_b(K)$

E_2

Emission

$E_2 = E_b(L) - E_b(K)$

Electrons, the Photoelectric Effect and Characteristic Fluorescence

Characteristic radiation

Incoming photon

M_α

L_α

N

M

L

K

L_β

e

e

e

e

e

e

e

K_β

K_α

Siegbahn Notation

Nomenclature

$AgK\alpha_1$

Element

Shell vacancy

Transition shell

Which energy

K

L_I
L_{II}
L_{III}

M_I
M_{II}
M_{III}
M_{IV}
M_V

$K\alpha_2$

$K\alpha_1$

$K\beta_1$

$L\alpha_1$

$L\alpha_2$

$L\beta_1$

K lines

L lines

Excitation / Emission of Characteristic X-ray Radiation

i.e. Cu – Absorption edge at 8.98

The Photoelectric Effect and Absorption Edges

X-Ray Absorption Spectrum of Barium
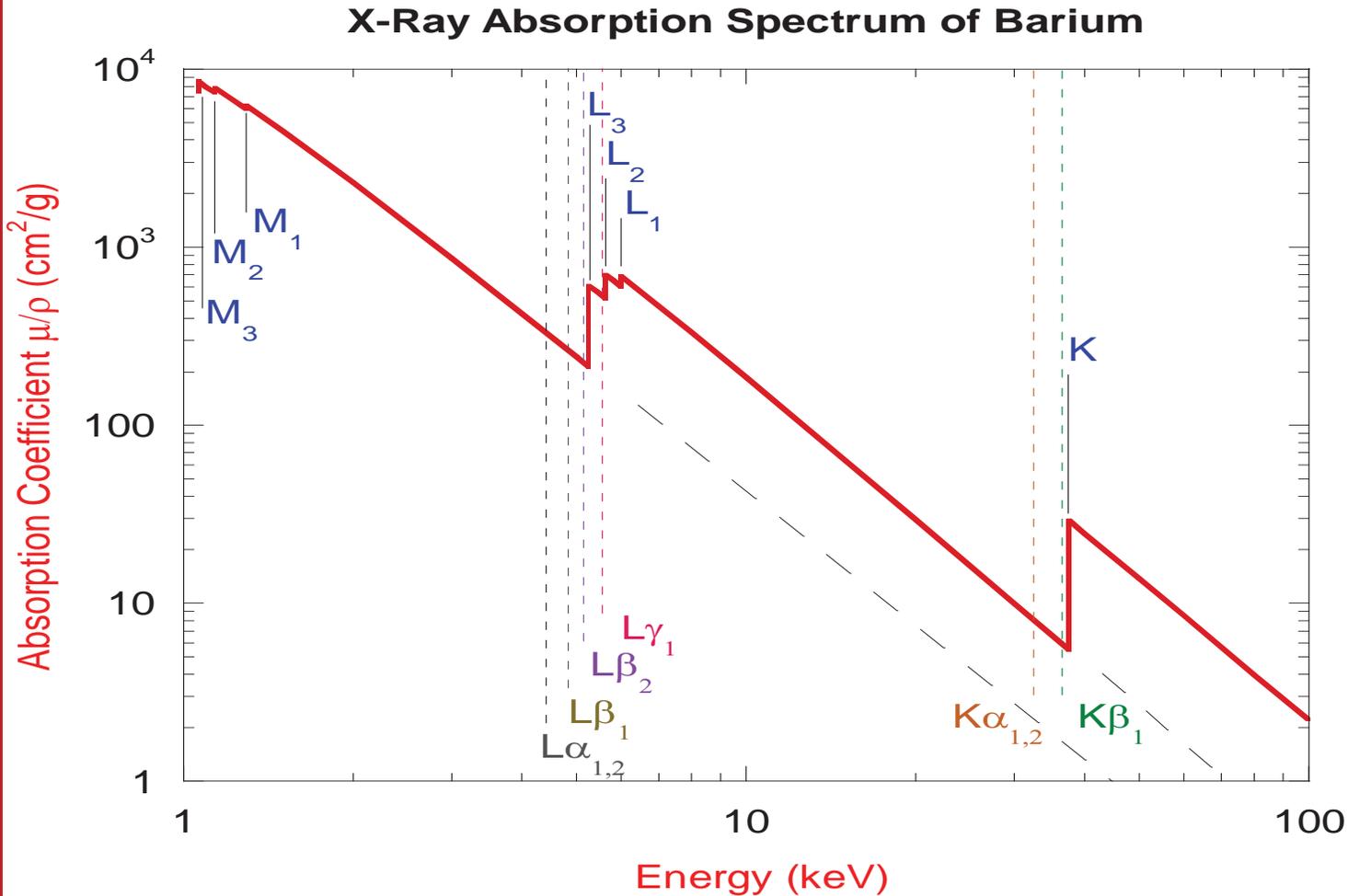
- Sudden jumps in absorption (edges) occur where the energy of the incident X-rays exceeds the binding energies of a particular electron state.
- The energy of a particular transition is always less than the energy of edge corresponding edge.
- Absorption is additive –photoelectric absorption from earlier edges is superimposed and hence the fluorescence spectrum will contain emission from all edges up to the energy of the incident radiation.

Electronic Transitions – Notation (Example: Barium)

Line	Siegbahn	Electron Binding Energies (keV)	Energy of emitted radiation (keV)	Wavelength (Å)
$K\text{-}L_2$	$K\alpha_2$	37.441, 5.634	31.807	0.390
$K\text{-}L_3$	$K\alpha_1$	37.441, 5.247	32.194	0.385
$K\text{-}M_2$	$K\beta_3$	37.441, 1.137	36.304	0.342
$K\text{-}M_3$	$K\beta_1$	37.441, 1.062	36.379	0.341
$K\text{-}N_2$	$K\beta'_5$	37.441, 0.192	37.249	0.333
$K\text{-}N_3$	$K\beta''_2$	37.441, 0.180	37.261	0.333
$L_3\text{-}M_1$	$L\alpha_1$	5.247, 1.293	3.954	3.136
$L_3\text{-}M_4$	$L\alpha_2$	5.247, 0.796	4.451	2.786

$$E = \frac{h \times c}{\lambda} = E_{keV} = \frac{12.4}{\lambda(Å)} = \frac{1.24}{\lambda(nm)}$$

or

$$\lambda(Å) = \frac{12.4}{E_{keV}} \qquad \lambda(nm) = \frac{1.24}{E_{keV}}$$

Energy (keV) = 12.4 ÷ wavelength (Å)

XRF Spectrum of Pure (98+%) Barium

$K_{\alpha1}$ 32.19 keV

$K_{\alpha2}$ 31.81 keV

$L_{\alpha1}$ 4.46 keV

$L_{\beta1}$ 4.83 keV

$L_{\beta3}$ 4.93 keV

$L_{\beta2}$ 5.16 keV

$K_{\beta1}$ 36.37 keV

$K_{\beta2}$ 37.35 keV

Counts/s

Energy keV

) X-Ray Data Booklet ✕ ＋

→ C ⌂ ⓘ xdb.lbl.gov

Free Hotmail | Suggested Sites | Web Slice Gallery | m Solomon Cousins Reu... | ❈ Kirkland Lake: A Jewis... | ISTG Vol 3 - SS Stava... | Scan for Privacy | Multivariate Analysis ...
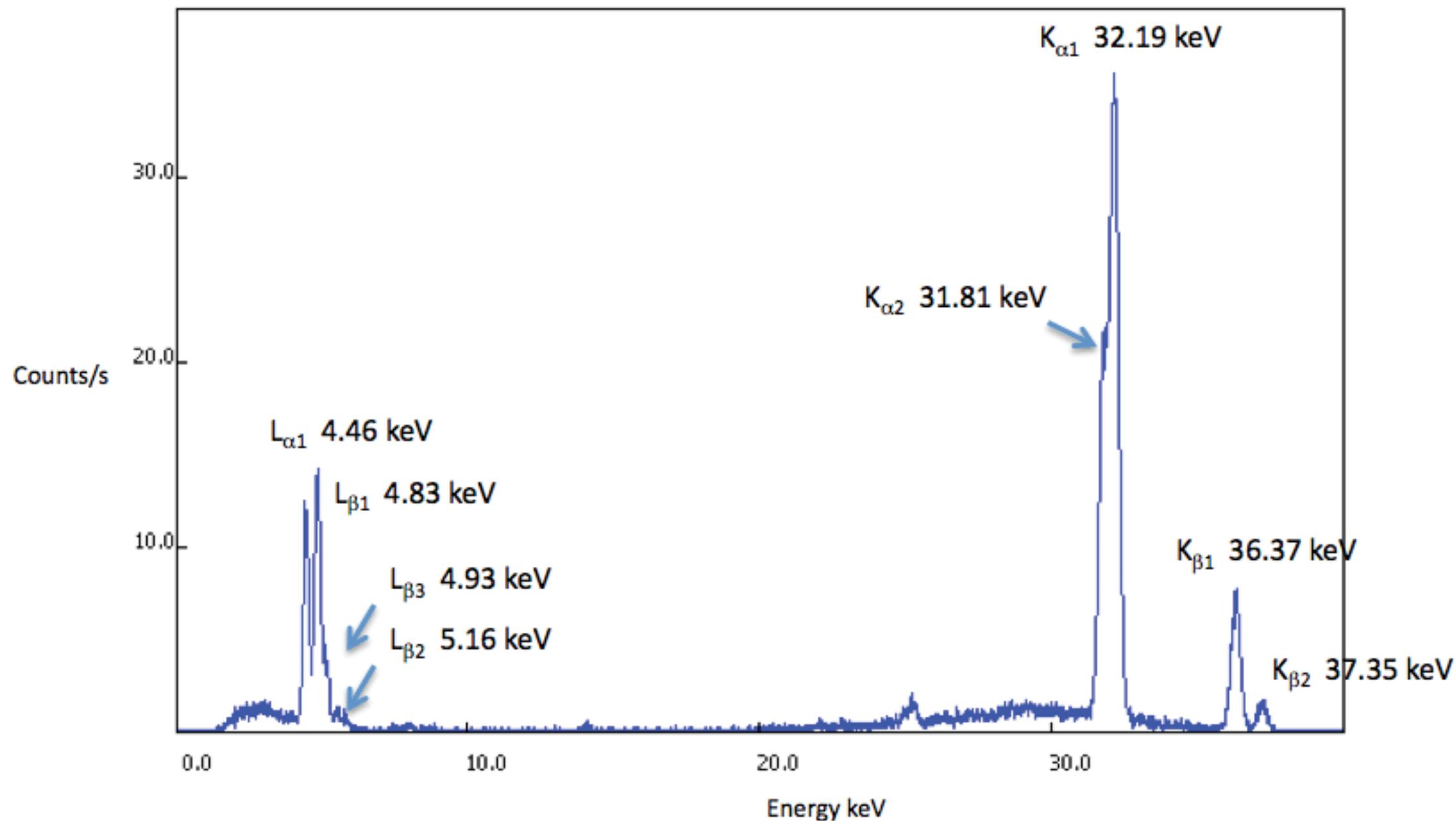
X-RAY DATA BOOKLET

Center for X-ray Optics and Advanced Light Source

Lawrence Berkeley National Laboratory

- **Introduction**

- **X-Ray Properties of Elements**

- **Electron Binding Energies**
- **X-Ray Energy Emission Energies**
- **Fluorescence Yields for K and L Shells**
- **Principal Auger Electron Energies**
- **Subshell Photoionization Cross-Sections**
- **Mass Absorption Coefficients**
- **Atomic Scattering Factors**
- **Energy Levels of Few Electron Ions**
- **Periodic Table of X-Ray Properties**

- **Synchrotron Radiation**

- **Characteristics of Synchrotron Radiation**
- **History of X-rays and Synchrotron Radiation**
- **Synchrotron Facilities**

- **Scattering Processes**

UPDATE *October 2009*

A new version of the booklet is now available!
Please visit the **CXRO** web site to obtain your copy.

X-Ray Data Booklet (October 2009)[pdf]

http://xdb.lbl.gov/

LBNL/PUB-490-Rev.2

Center for X-Ray Optics
and
Advanced Light Source

X-RAY DATA BOOKLET

Albert Thompson	Ingolf Lindau
David Attwood	Piero Pianetta
Eric Gullikson	Arthur Robinson
Malcolm Howells	James Scofield
Kwang-Je Kim	James Underwood
Janos Kirz	Douglas Vaughan
Jeffrey Kortright	Gwyn Williams
	Herman Winick

January 2001

Lawrence Berkeley National Laboratory
University of California
Berkeley CA 94720

Voltage setting and region of interest

x 1E3 Pulses

45 kV, 60 uA Cu/Ti/Al filter

Fe

Si

Rh

**10 kV, 120 uA no filter
No He flush**

Si

Fe

Rh

- keV -

Excitation / Emission of Characteristic X-ray Radiation

Emission

Bond energy of the electron

Absorption edge/ Excitation Potential

0

Energy of incoming photon

[keV]
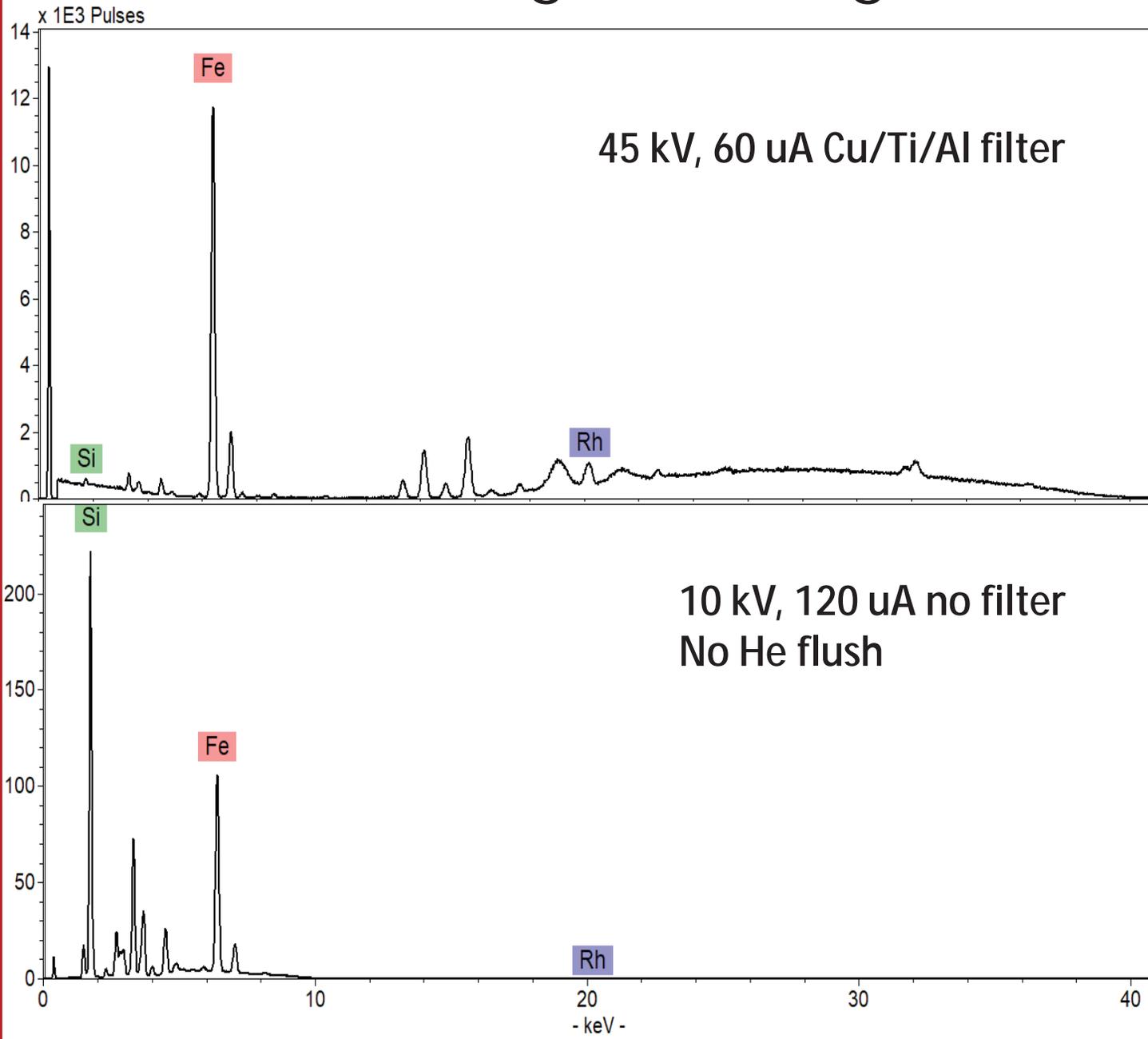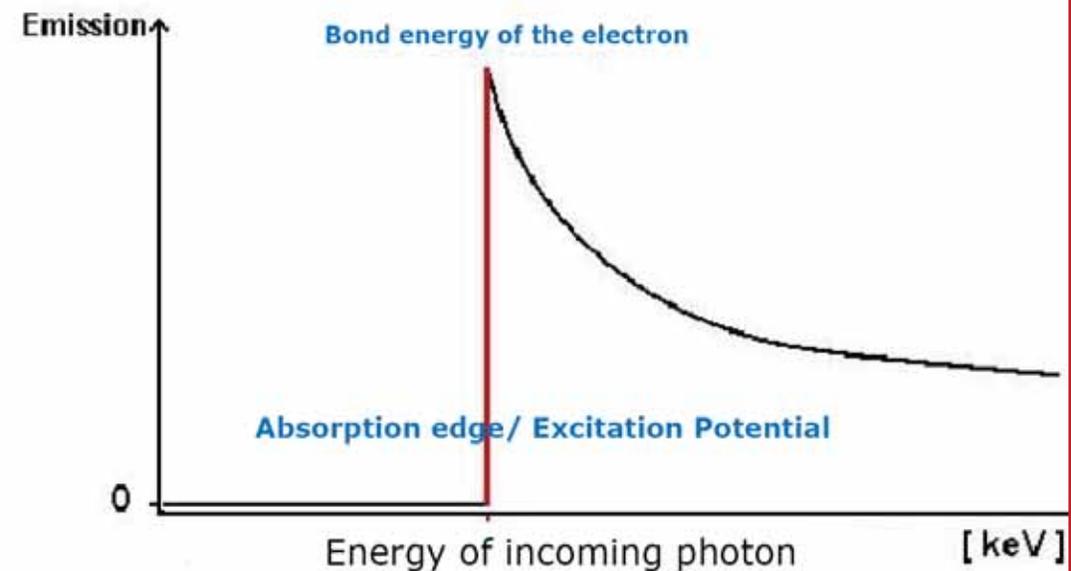
Theory: X-ray identification (open architecture)

- **"organic"** elements are not identified in spectrum (absorbed by air)
- **Low Z** elements only show K lines (L lines two low to be detected)
- **Medium Z** elements show both K and L lines
- **High Z** elements show L and some M lines (K can't be excited)

Bruker Tracer 5g
Can see F with He flush

Na can be identified with special instrumentation setup or with Tracer 5g

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114				

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Ceramics – complexity for analysis and approaches to achieving high quality data

Ceramic types

- Ceramic Bodies

Ceramic Bodies	Porosity	Firing Temp	Comment
Terra-cotta	High ~30%	well below 900	Unglazed, coarse fabric
Earthenware	~10-25%	900-1200	Glazed or unglazed, non vitrified
Stoneware	~0.5-2%	1200-1350	Glazed or unglazed, vitrified body
China	~<1%	1100-1200	White fabric, vitrified
Porcelain	Near 0%	1300-1450	Hard body, translucent, fine fabric

- Ceramic composed mainly of aluminosilicates (kaolinites smectites, montmorillonite and vermiculites)

Earthenware

http://www.mfa.org/artemis/zoom.asp?oid=315436&pic=SC37245.fpx&tem=1

China

http://netra.glendale.cc.ca.us/ceramics/bowkakiemonplate.html

kaolinite

O
OH
Al
Si
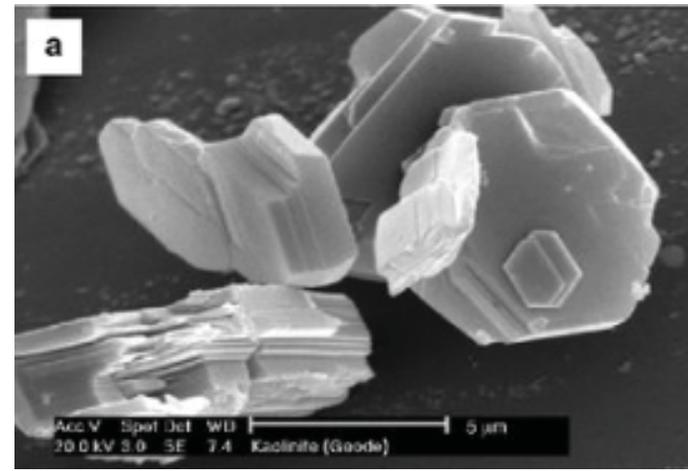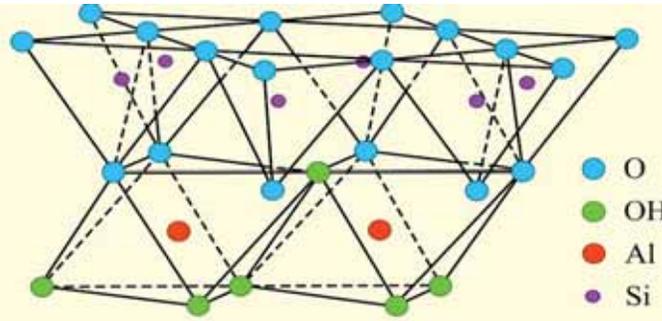
Typical elements of interest in ceramics analysis
(Yellow = major, Red = trace)

Periodic Table of the Elements

Heterogeneity of Ceramics

- Variable particle size based on –
  - Fabric type
  - Temper
  - Mineral inclusion
  - Firing temperature – vitrification
  - Porosity
  - Etc..
- Potential for variable surface chemistries
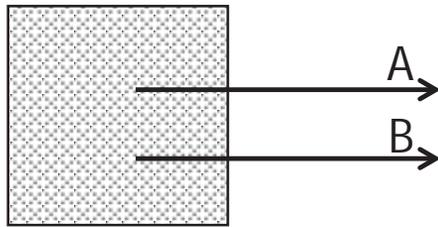- Increased Matrix effect possible

Gašparič, Andreja Žibrat. "A new look at old material: ceramic petrography and Neo\Eneolithic pottery traditions in the eastern Ljubljansko barje, Slovenia." (2013).
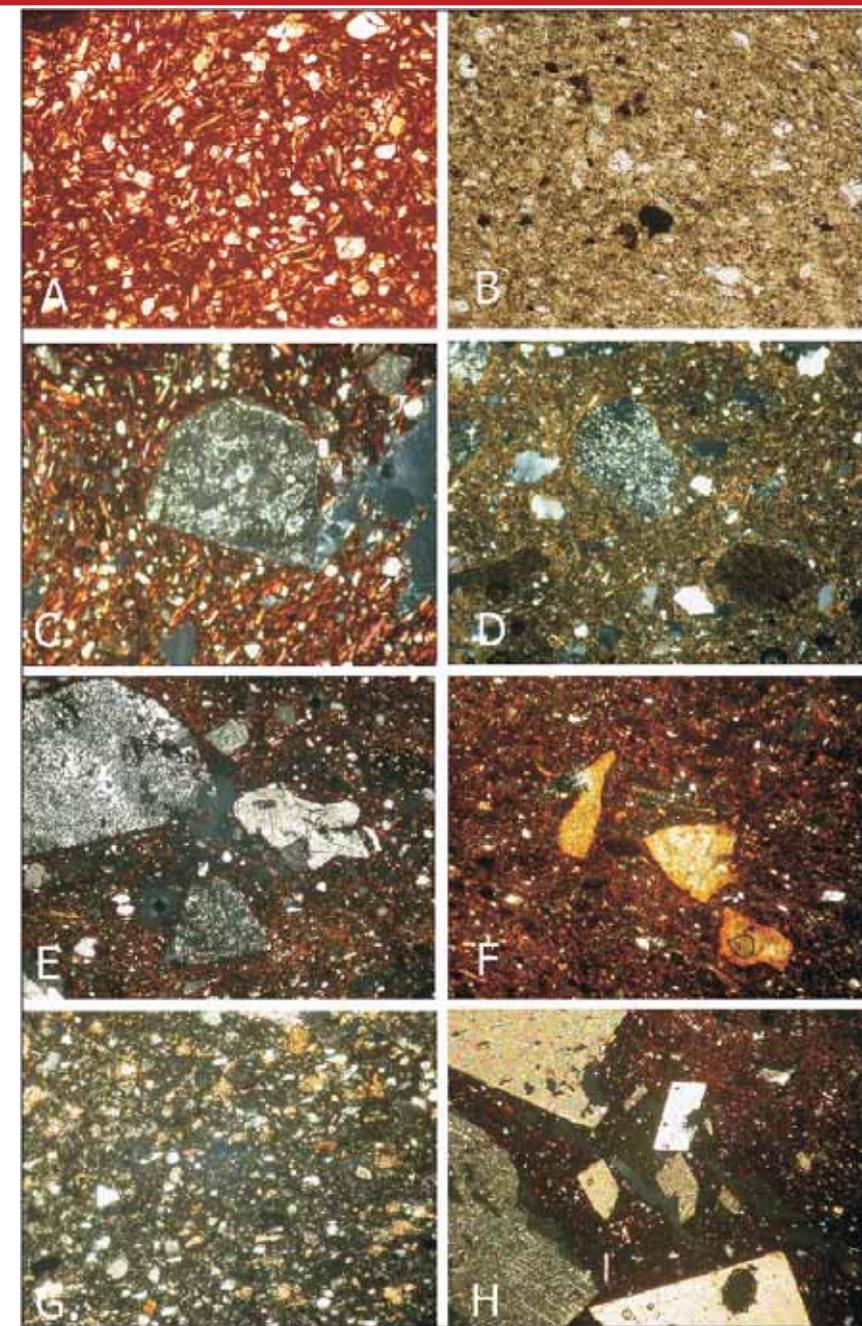
Importance of homogenization

Specimen Heterogeneity
(Variable particle size and distribution)

Specimen Heterogeneity
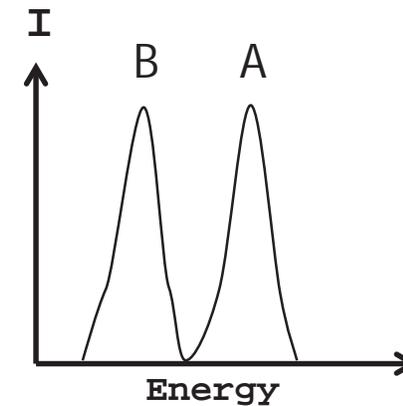**(Layered Structure)**

i.e.
- Porosity
- Coarse ceramic body
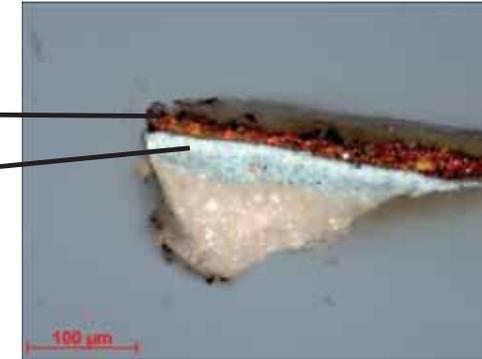
i.e.
- Corroded Material
- **Surface alterations**
- Layered structures

Homogenize

Homogenize

Homogenous Sample
(Powdered or Fused)
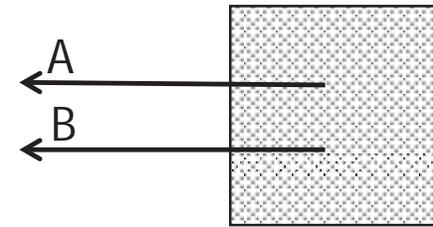
Homogenous Sample
(Powdered or Fused)

Heterogeneous materials allow for additional attenuation altering resulting peak height – thus changing the reported chemistry

X-ray physics - Quantification

Physics calculations based on **homogenous** materials that are **infinitely** thick.

"In practice, however, there are two major constraints that may prevent this ideal circumstance (*quantification*) from being achieved, these being sample size and samples heterogeneity" (Jenikins 1999: 141).

Samples prepared from heterogeneous materials require significant pre-treatments prior to analysis
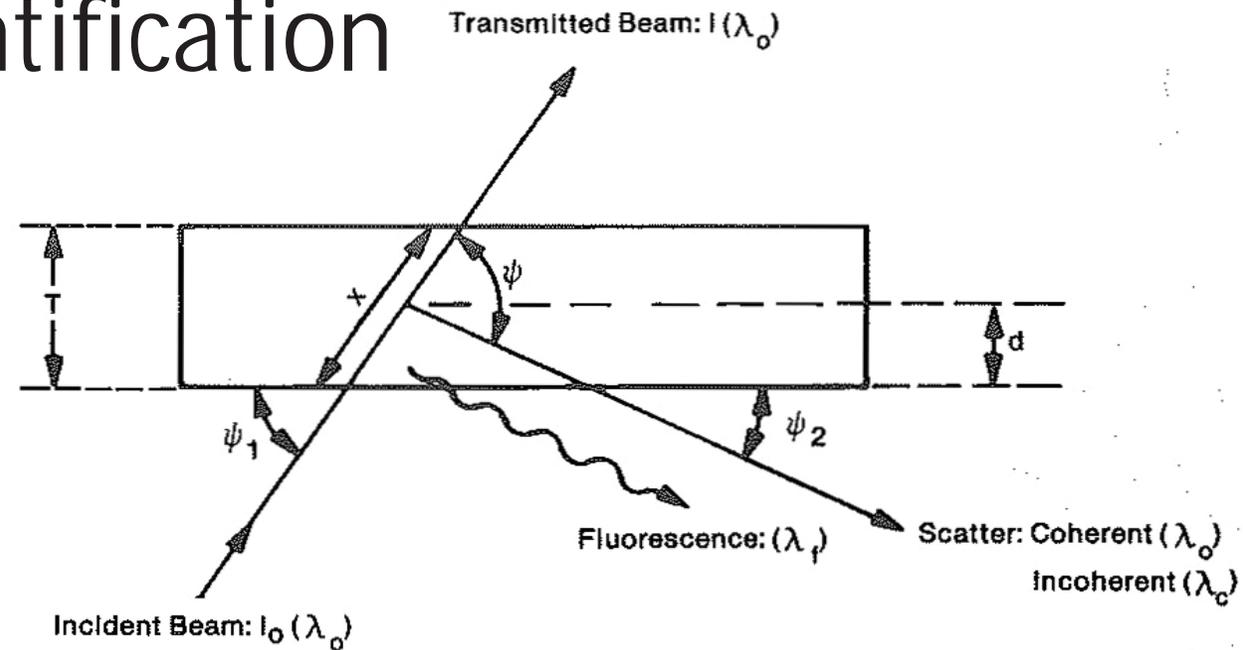
T = Sample Thickness
x = Path Length
d = Penetration Depth
ψ_1 = Incident Angle
ψ_2 = Take-Off Angle
ψ = Scattering Angle
μ = Mass Absorption Coefficient
ρ = Density

- Transmitted Beam Intensity: $I(\lambda_o) = I_o(\lambda_o) \exp(-\mu\rho x)$
- Incoherent Scatter Wavelength: $\lambda_c - \lambda_o = 0.0243 [1 - \cos\psi]$
- Fluorescence Penetration Depth: $d = x \sin\psi_2$

Figure 1.3. Interaction of the primary X-ray beam with the sample.

From Jenkins 1999

Change in surface chemistry due to deposition

- First pointed out by Sayre, Dodson and Burr Thompson in 1957.

- Alkali and alkali-earth metals are most reactive with water and typically the most mobile— Leaching of cesium and strontium (among others) noted in low-fired ceramic.

- Reduction of Ca, Cs, Rb, K, and Na at surface.

- Vitreous phases are prone to breakdown and leaching as glass would.

- Dependent on many factors - pH, redox conditions, organic activity etc…

- Mobile soluble salts.

DESALINATING ARCHAEOLOGICAL CERAMICS
December 20, 2013 · by Sarah Klopf -
https://rammleventisproject.wordpress.com/2013/12/20/desalinating-ceramics/
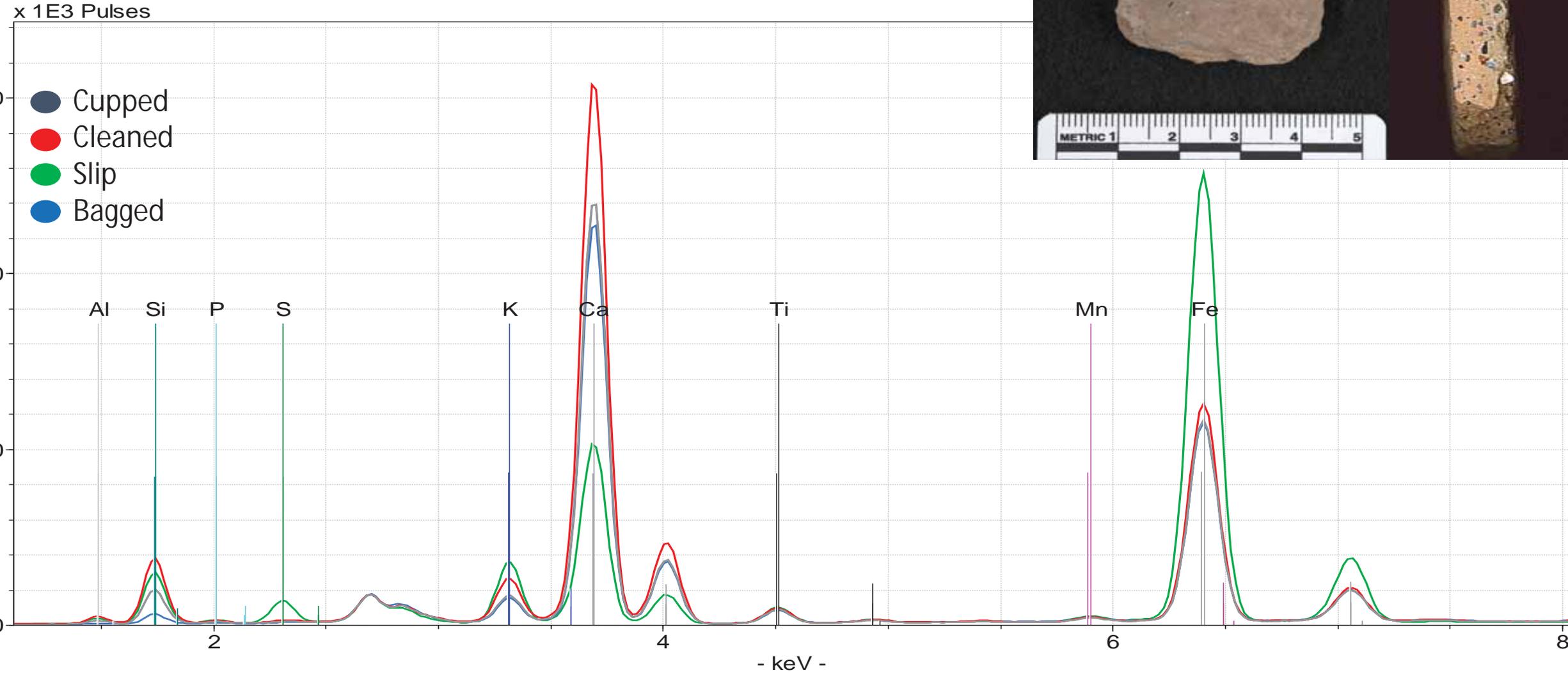
Schwedt, A., Mommsen, H. and Zacharias, N., 2004 *Archaeometry*, *46*(1), pp.85-101
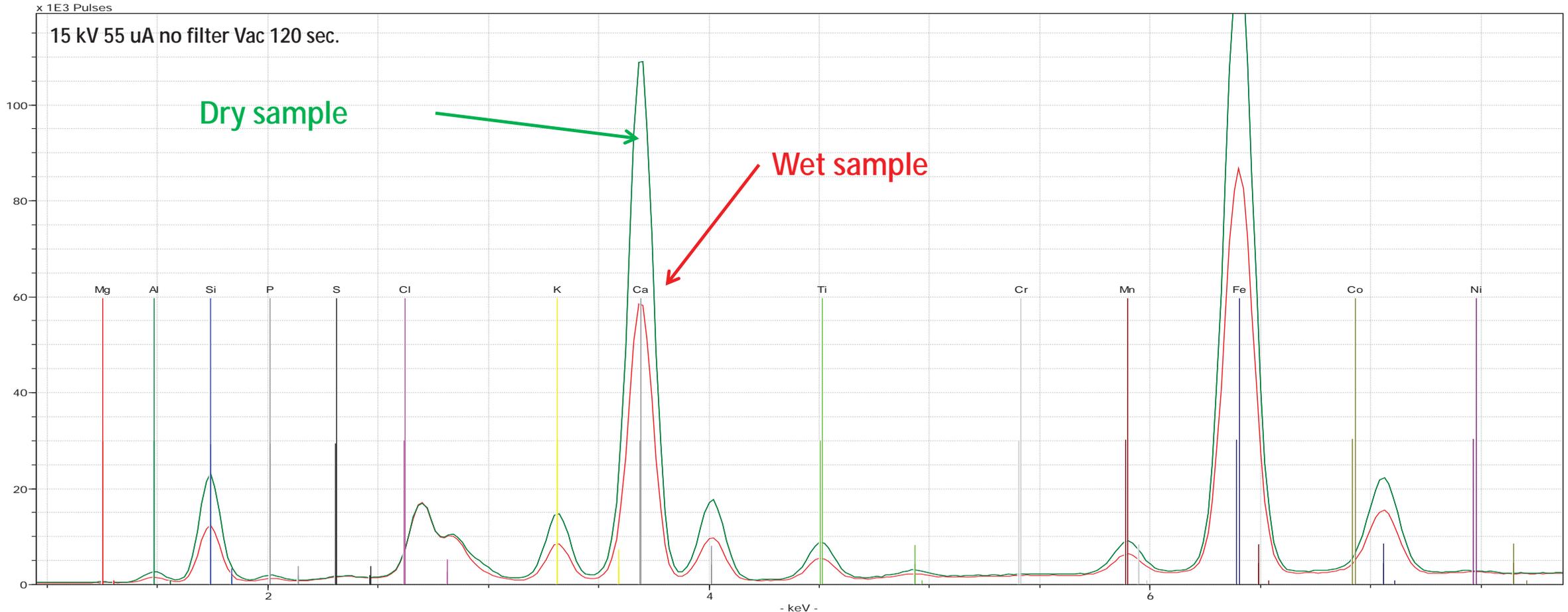Buxeda iGarrigóset al. 2001, 360–2.
Golitko, M., Dudgeon, J.V., Neff, H. and Terrell, J.E., 2012 *Archaeometry*, *54*(1), pp.80-100.

Sample 1	Al	Si	P	K	Ca	Fe
Crushed cupped	1.4	8.3	0.13	1.35	15.78	2.65
Cleaned	3.46	12.85	0.29	2.07	21.05	2.74
Red Slip	2.91	13.43	0.41	3.71	8.1	6.09
Crushed bagged	-0.37	3.51	0.02	1.18	14.18	2.44

Effect of Moisture on calibration

15 kV 55 uA no filter Vac 120 sec.

Dry sample

Wet sample

- Dry = Green: Wet = Red normalized to Rh La

- Note the increased area under peak for all light elements with dry sample. Trace elements of Mg, Al and P **highly attenuated** by the addition of water.

- The resulting quantification would be a **52%** decrease for **Al** and a **47 %** decrease for **P**.

Overcoming heterogeneity and surface alterations

- Create standards (reference materials) that
  - a) **Match** the composition (dynamic range and all elements present),
  - b) have **similar matrix** and **particle size** to the samples.
- Only when they are prepared in the same way can you hope to create a more linear relationship used for calibration.
- When standards (reference materials) and samples are prepared the same way, **ONLY then**, can you achieve accuracy and precision in calibration.
- There is **no substitute** for good sample preparation. If the sample is poorly prepared **NO AMOUNT OF CORRECTION** can improve the analytical results. Time and resources should be devoted to sample preparation to benefit fully from an XRF spectrometer.

Quantification – background, issues and application to ceramics
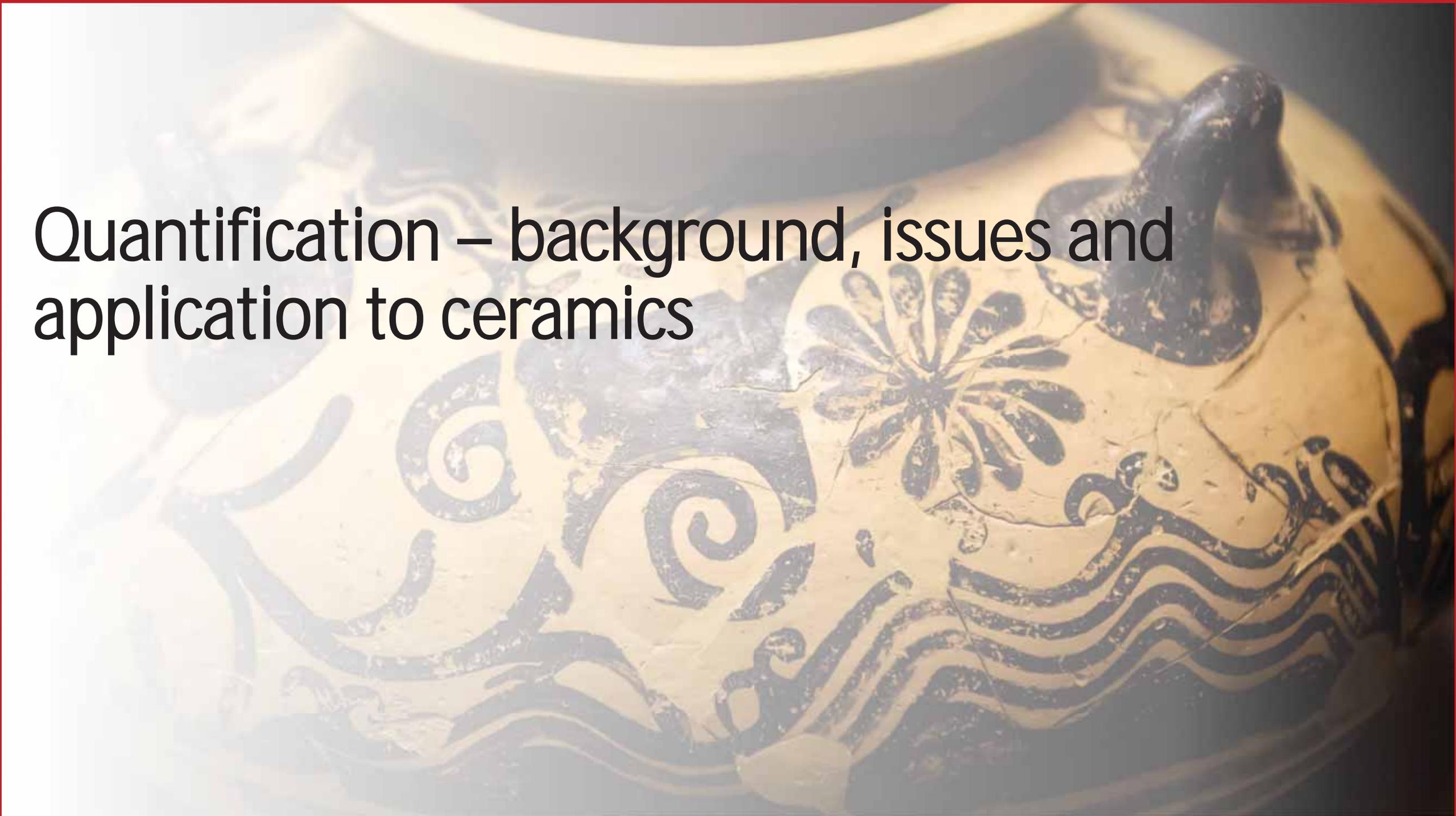
XRF quantification

Assumed factors (infinitely thick samples)

- Samples are **homogenous**
- Samples have similar – **small particle size**
- Samples have **flat smooth surfaces**
- Samples have similar **density** to each other **AND** the reference materials used for calibration.
- Samples are '**infinitely thick**' (for bulk samples)
- Samples are **large** enough to cover X-ray beam
- Samples are **dry**
- Samples are **not porous**
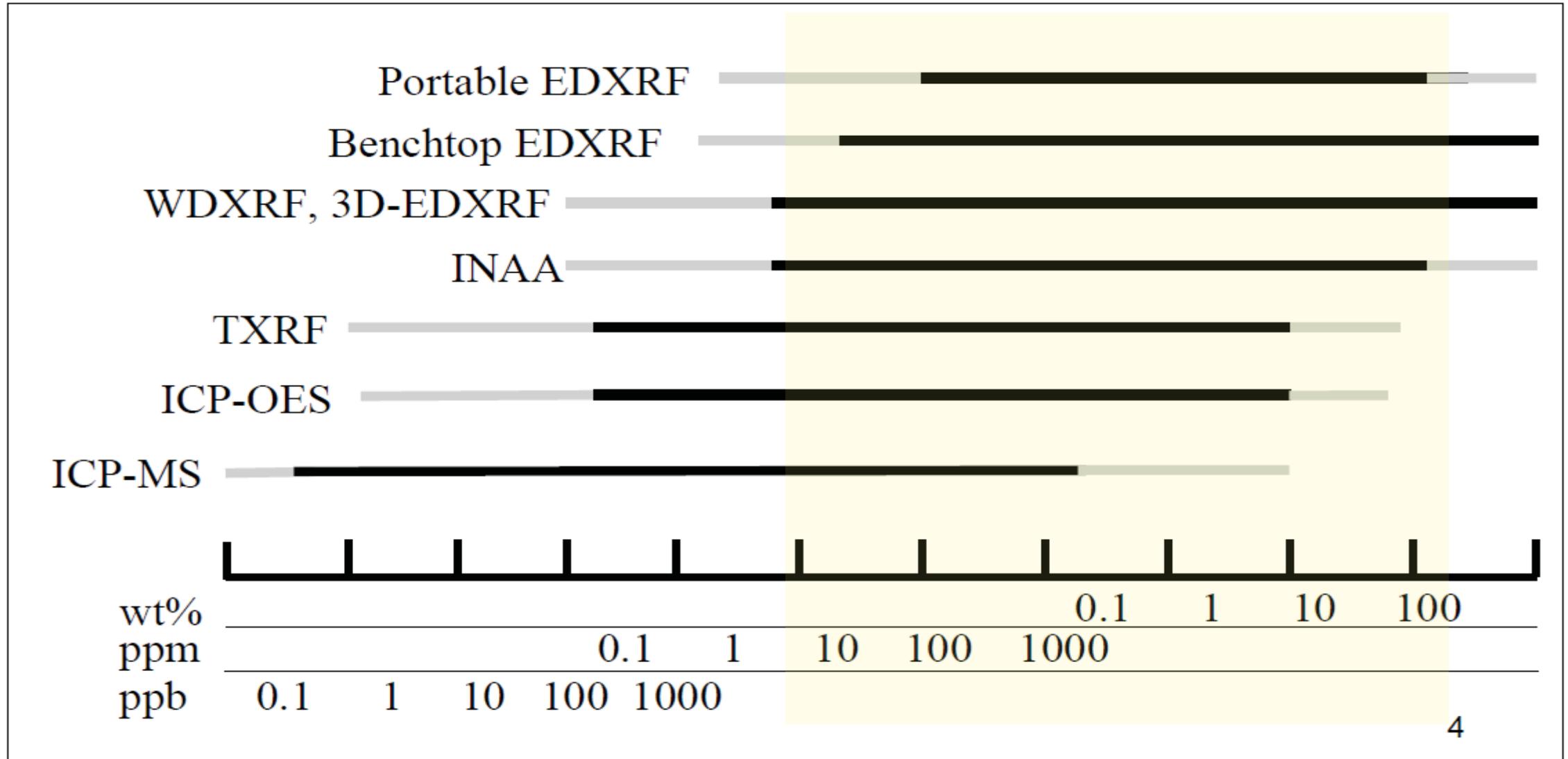
Dependent on several factors:

- Analyte **concentration**
- The **matrix**
- Accompanying elements **(matrix effects**)
- Sample type (solid, liquid, powder, fused etc...)
- Method of **sample preparation**
- Shape, thickness
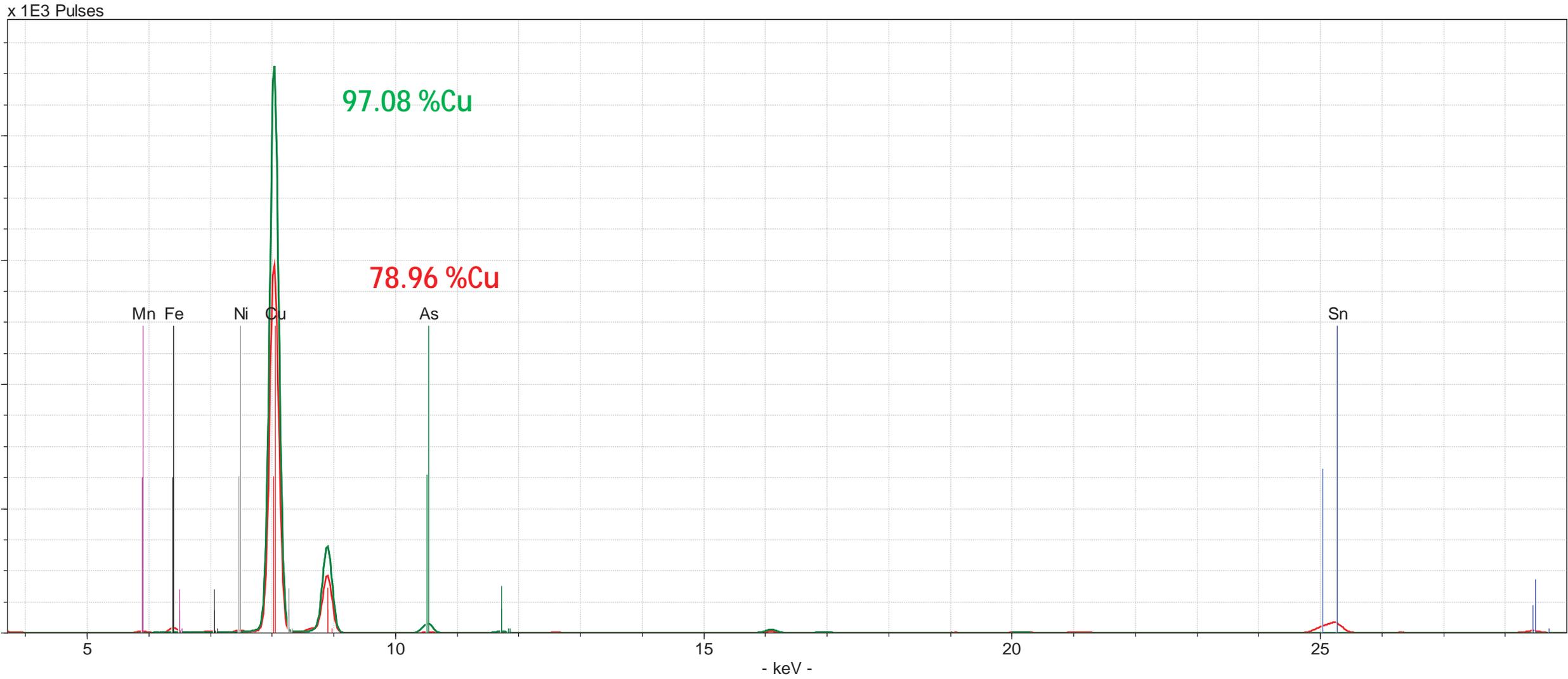- Instrumentation setup (geometry, spot size etc..)

Typical XRF metal reference standards: thick, flat, smooth and homogenous.

Typical analytical range


Legend:
- Measured readily
- Measured with difficulty

Methods (top to bottom): Portable EDXRF, Benchtop EDXRF, WDXRF, 3D-EDXRF, INAA, TXRF, ICP-OES, ICP-MS

Scale:
- wt%: 0.1, 1, 10, 100
- ppm: 0.1, 1, 10, 100, 1000
- ppb: 0.1, 1, 10, 100, 1000

4

Quantification: Peak height directly related to concentration

	Mn	Fe	Co	Ni	Cu	Zn	As	Pb	Ag	Cd	Sn	Sb
Red	0.72	1.20	0.14	0.50	78.96	0.49	0.06	0.26	0.10	0.15	16.05	0.66
Green				0.00	97.08		2.90	0.00			0.01	

Methods offered to achieve quantification
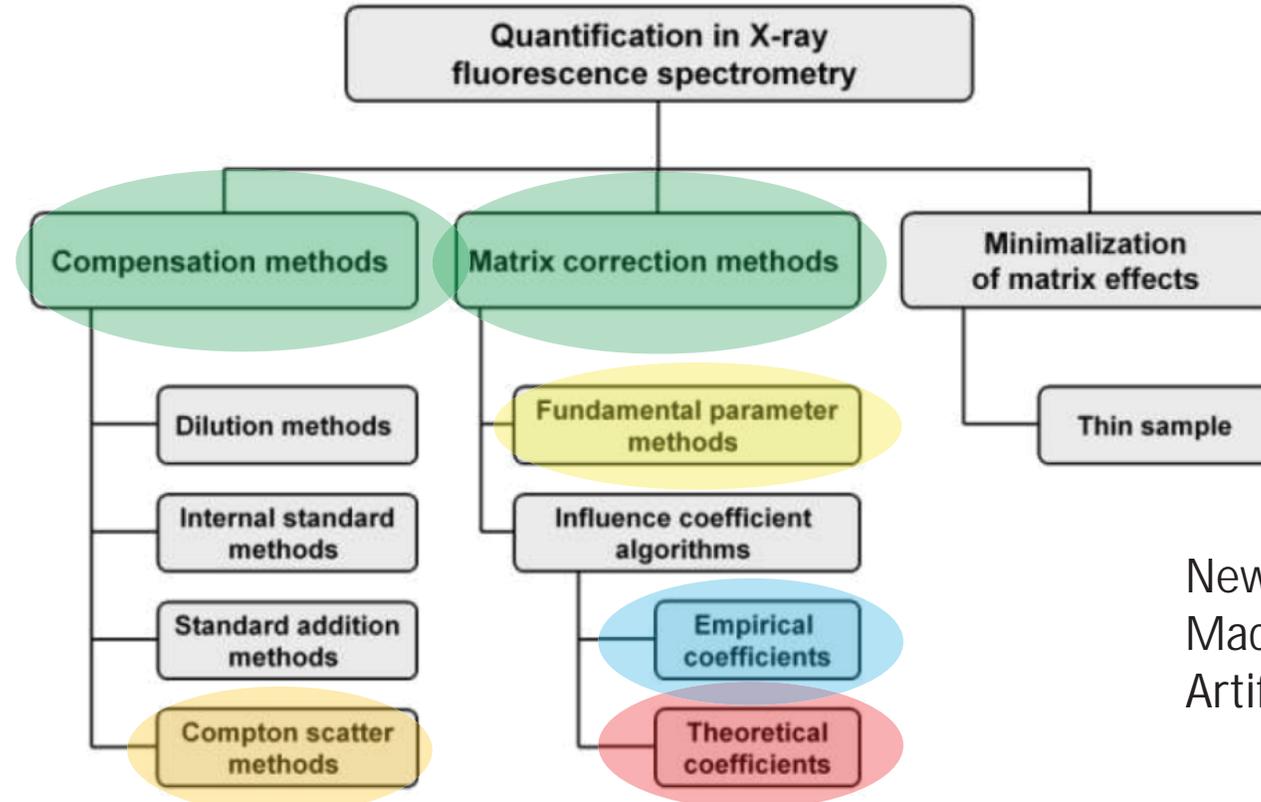
Newer approaches include:
Machine learning and
Artificial intelligence algorithms

- **Fundamental parameters**
  - Assumes:
    - Homogenous matrix
   - Values total 100% (usually)

Empirical calibrations

- **Compton normalization**
  - Assumes:
    - Lighter element composition
   - Values provided in ppm or volume/area (usually)

Theoretical calibrations

Accuracy, Precision and Bias

- **Accuracy** : Accuracy is a measure of how **close** the measured value is to the true value.

- **Precision:** Precision is a measure of the **agreement** among a group of individual measurements. (How close repeat measurements are to one another.)

- **Bias:** Bias is due to **systematic errors** such as a change in voltage since calibration or wrong calibration constants would introduce a constant error into each measurement. Bias can be reduced by calibration and carefully following established measurement procedures.
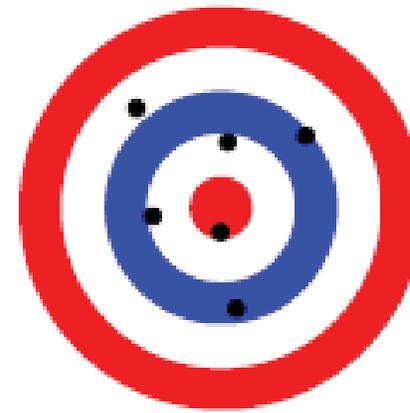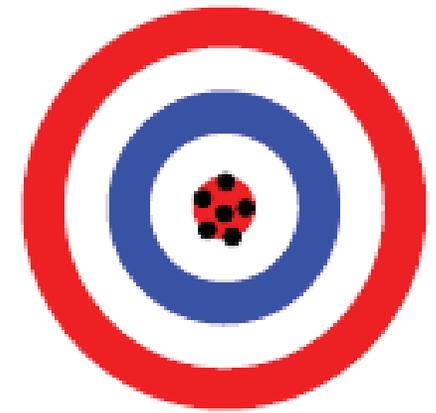
1
Unbiased
Imprecise
Inaccurate
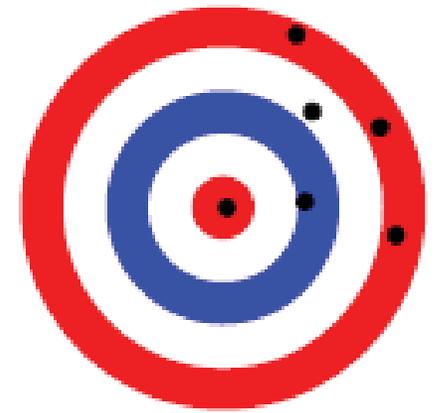
2
Biased
Imprecise
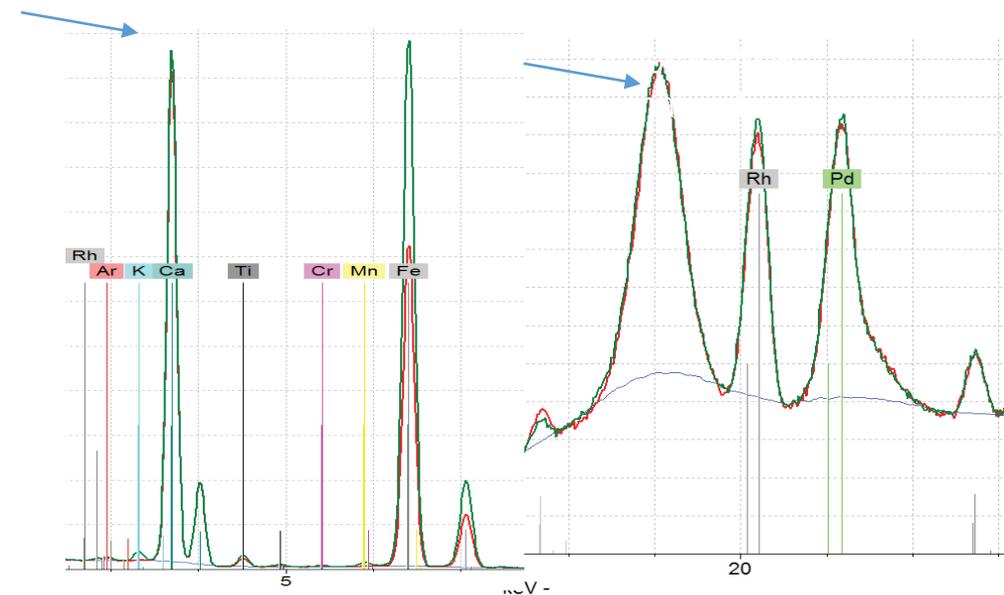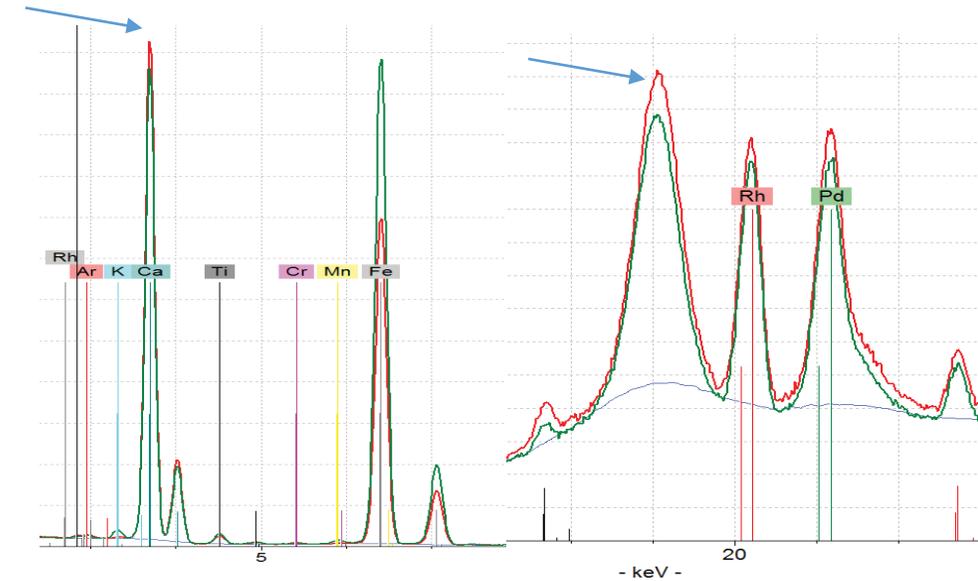Inaccurate
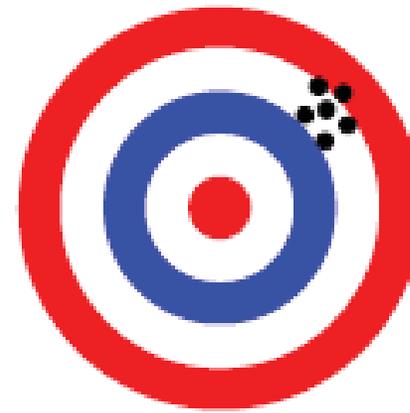
3
Biased
Precise
Inaccurate

4
Unbiased
Precise
Accurate

Matrix Corrections – Compton Normalization

- Based on the Compton scattering where Compton scatter is used an internal standard and a matrix correction.

$$I \,/\, I \text{ Compton} \sim C \text{ (+ corrections)}$$

- Matrix related corrections are calculated based on known concentrations and are determined based on calibration using standards (i.e., Fe, As_2O_3).

- The intensity of the Compton scatter can be used to obtain an estimate of the absorption coefficient of the specimen.

- Best for Z >23 and for samples that are relatively low density and samples containing relatively low concentrations of elements (i.e., soil, **potentially ceramics**).

Matrix Corrections – Fundamental Parameters

- Fundamental parameters (FP) calibrations are typically very accurate if the intensities of all matrix elements can be determined, or if the matrix of a sample is known.

- Calibration is **KEY** to success – either through pure-element standards, or through theoretical calculations (standardless analysis).

- Can greatly improve results by using (one or many) standard reference material(s) during calibration.

# Matrix Corrections – Fundamental Parameters

Advantages

- Method can be applied to any sample type
- Do not need to use standards (expensive to purchase)

Disadvantages

- Do not consider all physical interactions (i.e. tertiary fluorescence, scatter of low Z elements etc.)
- Strongly dependent on **consistent** mass attenuation coefficients, fluorescence yield, instrument geometry tube energy etc...
- Can only be applied if **ALL** the elements in the sample are identified (low Z elements like C, O, N should not be present).
- Often assumes normalization to 100%
- Not reliably consistent between instrumentation (even with same calibration).

Egan Range Sr-Zr

Instrument
× Delta
● Omega
◆ WD
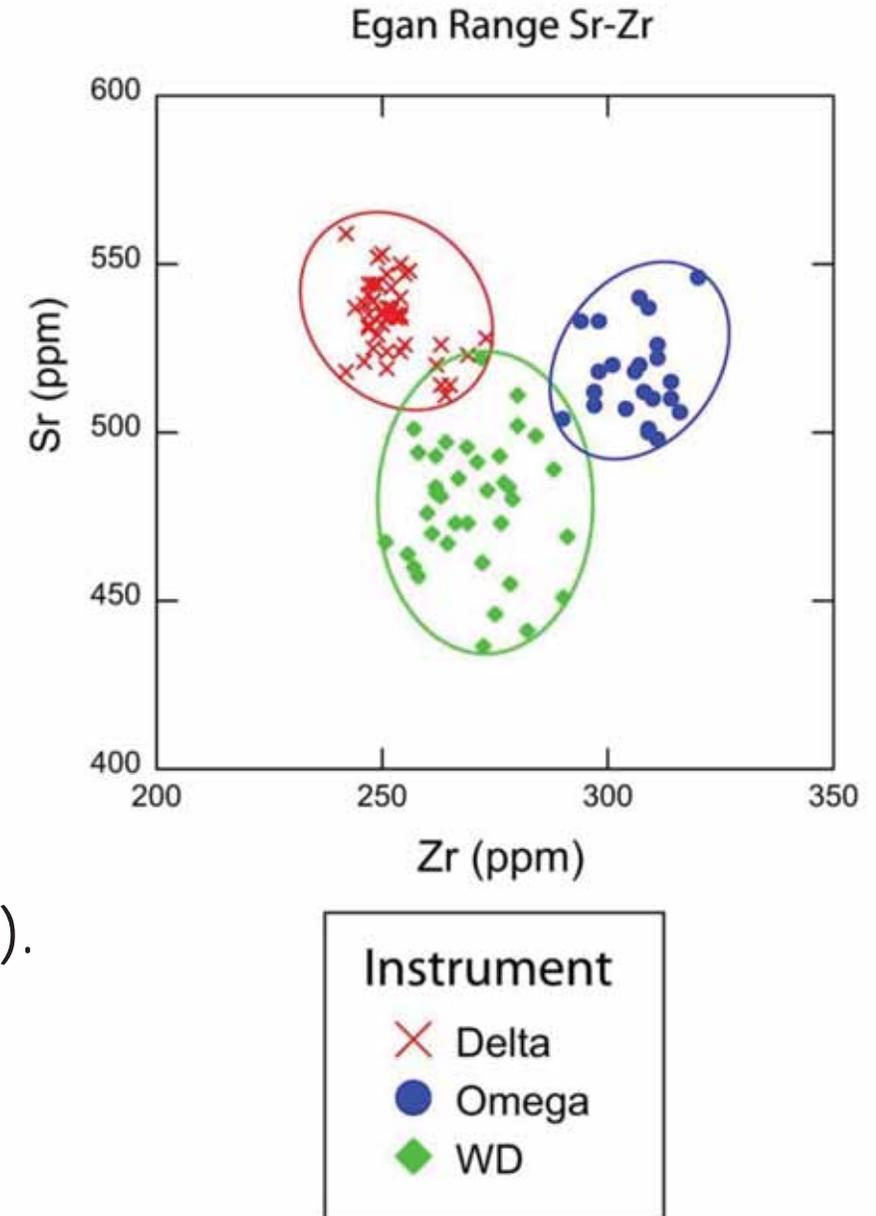
FP misidentification/peak overlap
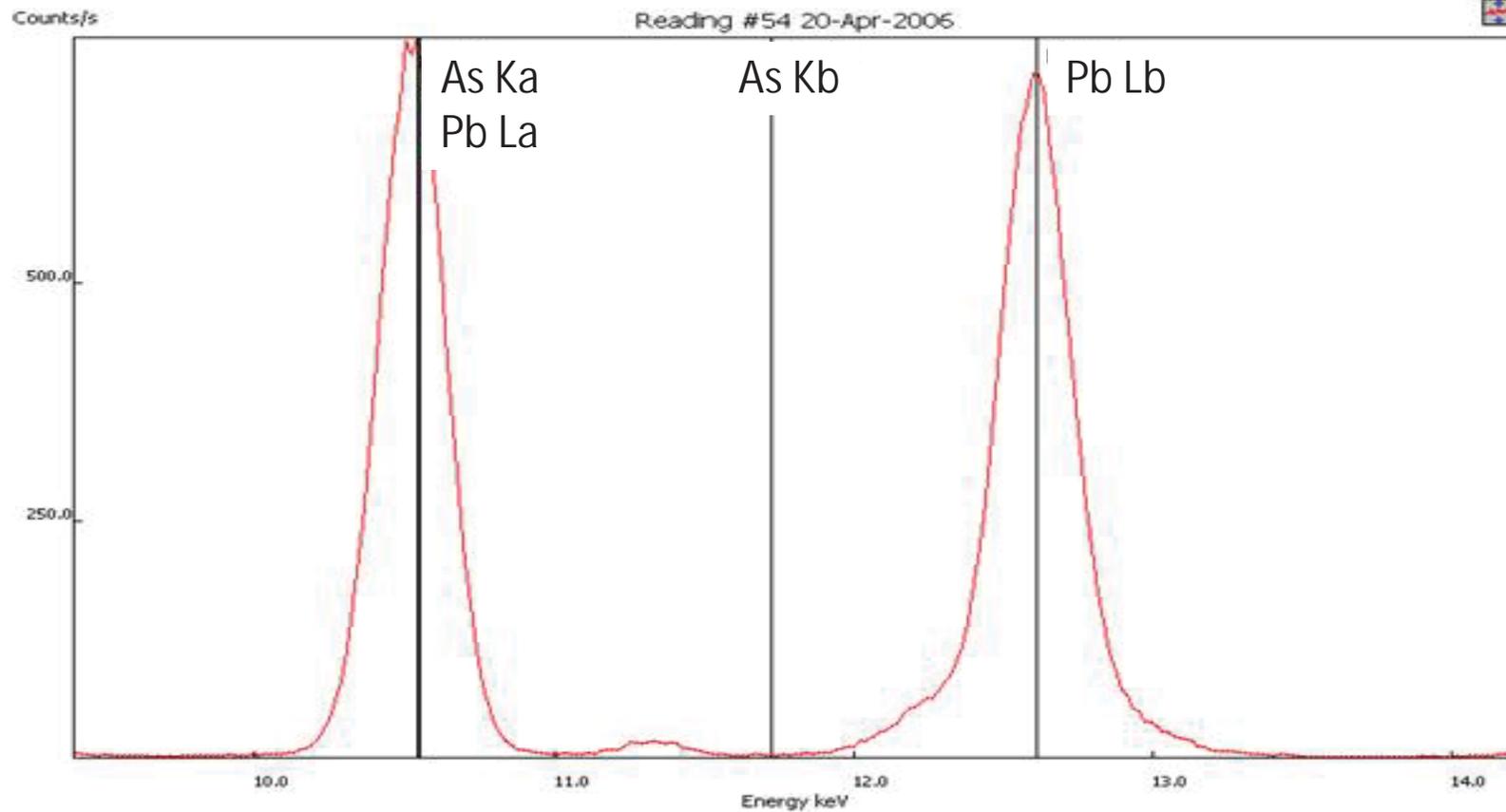
Reported Results (in ppm)

Ti	Cr	Fe	Zn	As	Ag	Cd	Sn	Pb
18992	2360	2472	436	50637	2776	764	1654	476703

Matrix Corrections – Influence coefficient algorithms

- Uses the relationship between counts and concentration (simple linear calibration curve). Matrix effects can affect a good linear calibration curve but can be compensated for with 'correction' models called empirical or theoretical coefficients.

$$C \sim I \text{ (+ corrections)}$$

- This method can be very accurate – only limited by experimental design.

- Can provides **more accurate results** than FP and Compton Normalization.

- Preparation of reference materials manufactured of the element(s) of interest in a matrix that **closely approximates** that of the unknown samples is necessary.

- The matrix correction and calibration are clearly seen so interpretation of the method is easy.
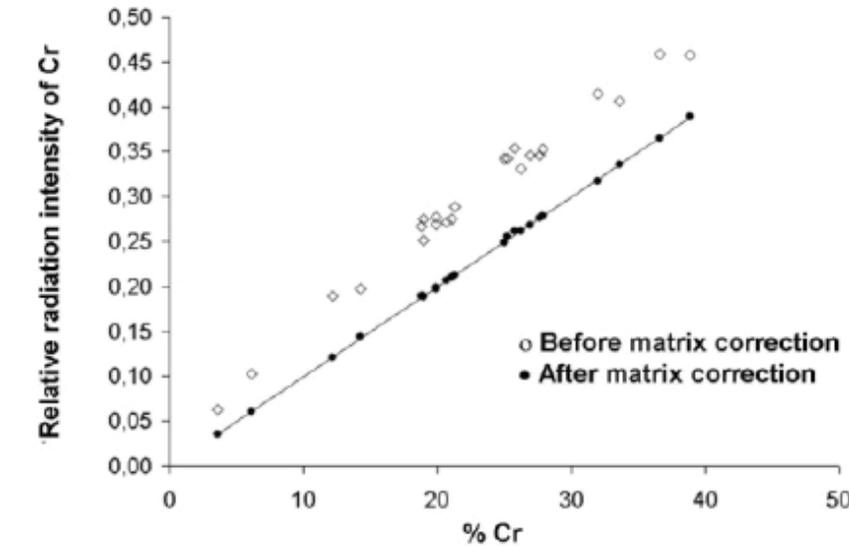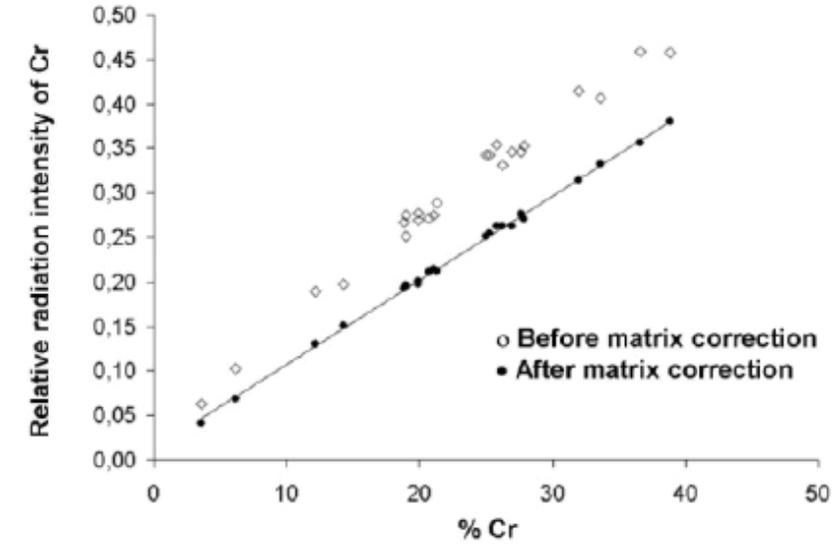
(a) Lachance-Traill algorithm and (b) Claisse-Quintin algorithm - Sitko and Zawisza, (2012)
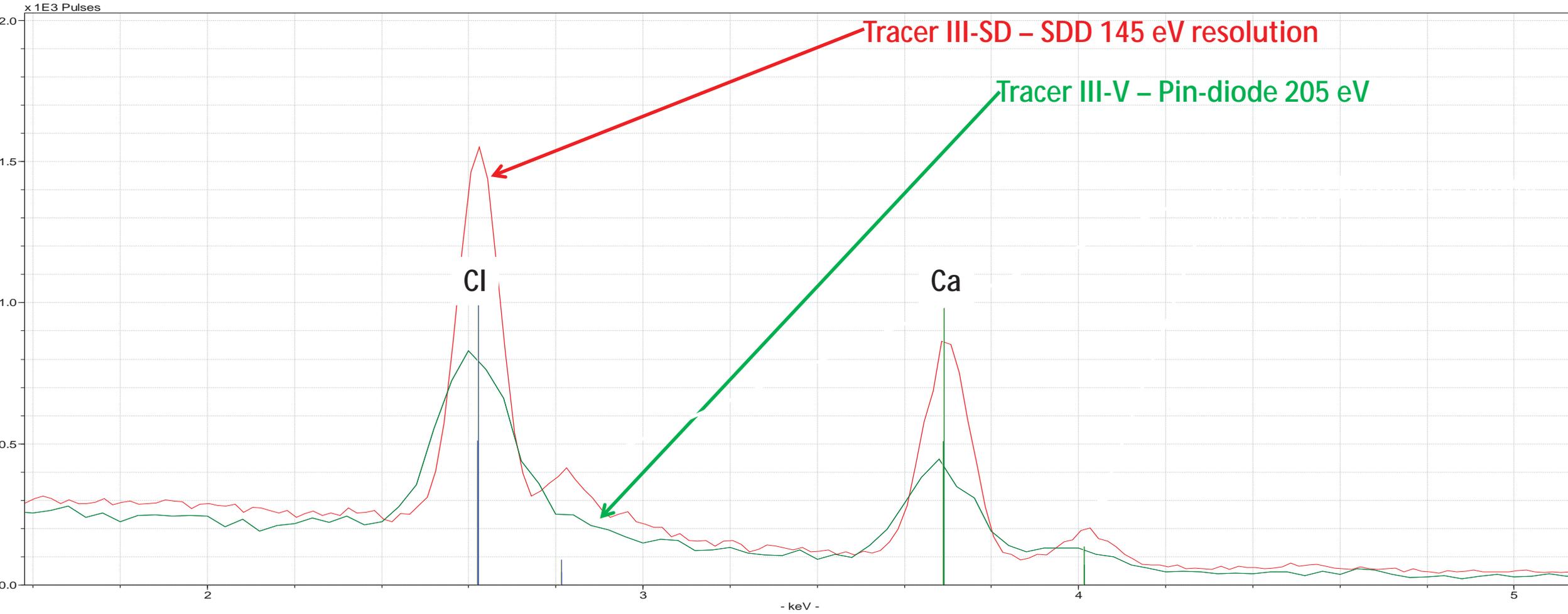
Spectral Interference Effects on calibration

Spectral interference – peak overlap – can lead to increased error in the calibration curve as well.
Think of $CuK\beta$ and $ZnK\alpha$, or $PbL\alpha$ and $AsK\alpha$.
This error is improved with increased resolution – SDD detector (~145eV) vs SiPin detector (~205eV).
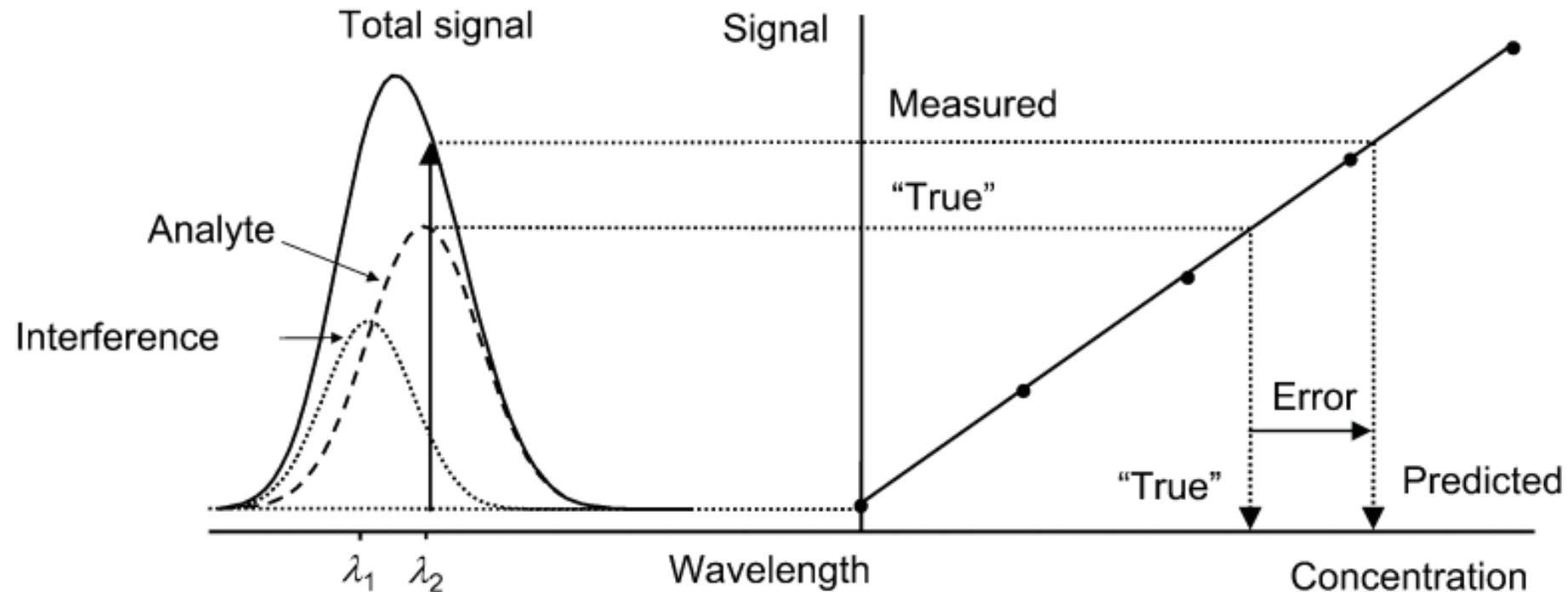
Increased resolution in new detectors to help with peak overlap

Difference in resolution between a standard Pin diode detector (Green) and an SDD detector (Red). Typical pin diode resolution at **205 eV** while SDD at **145 eV** at MnKa

Issues related to achieving quality quantification

- Matrix Issues
- Surface Roughness
- Particle Size Effects
- Heterogeneity
- Mineralogical Effects
- Curvature
- etc...

Poor Analytical Accuracy

Section of a Chalcolithic crucible showing high porosity, organic and inorganic temper and potential alteration to surface chemistry
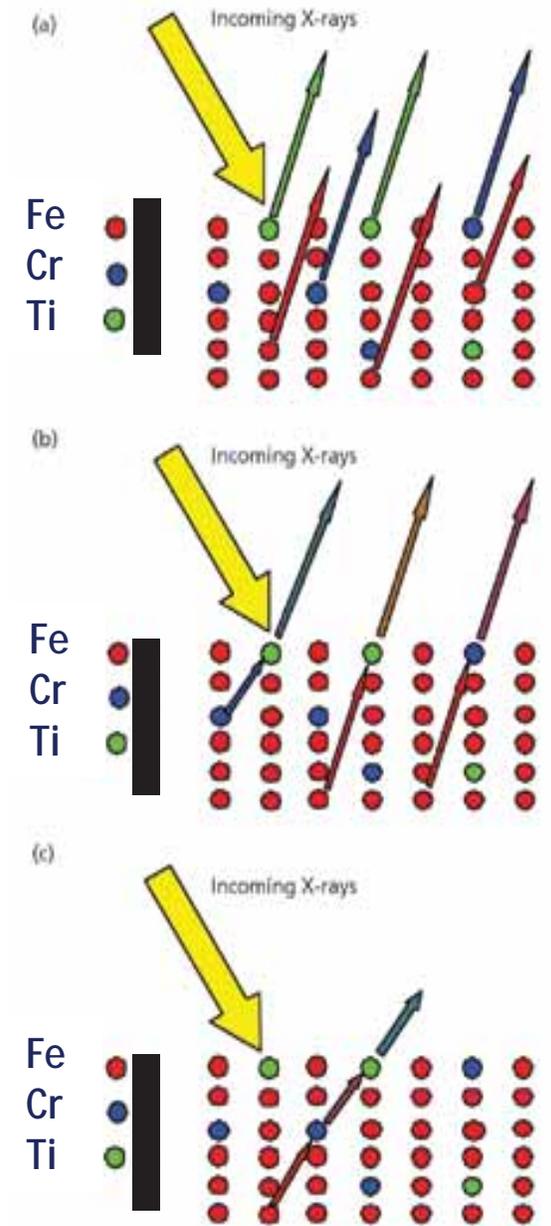
Matrix Effects on calibration

- Matrix effects are caused by the absorption and enhancement of characteristic x-ray photons within the sample.
- Can cause alteration to linear relationship established with pure element calibrations.
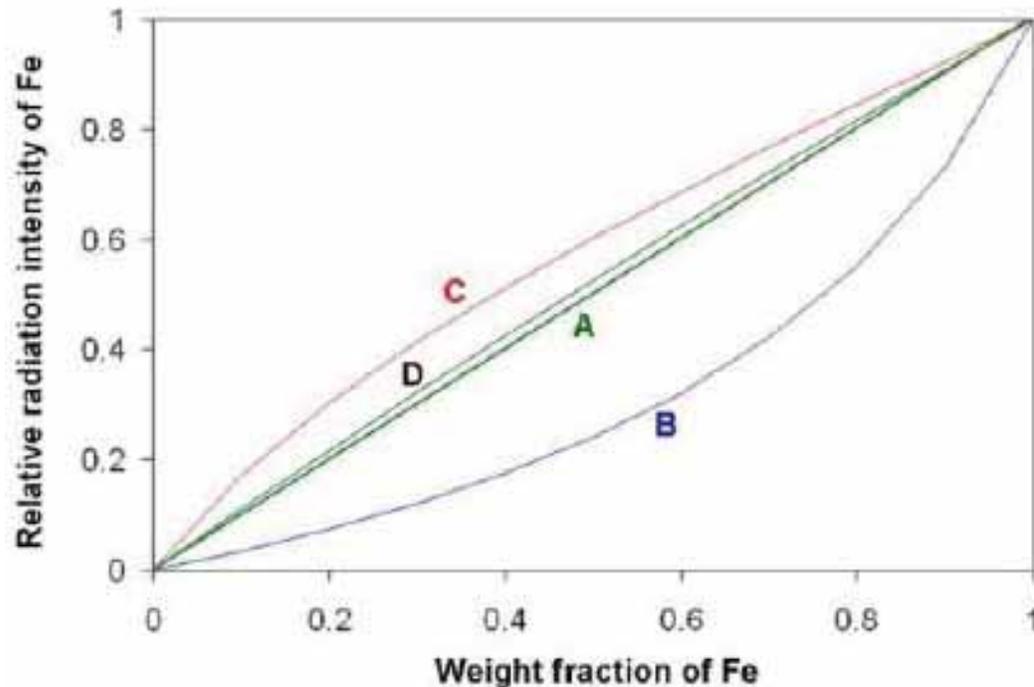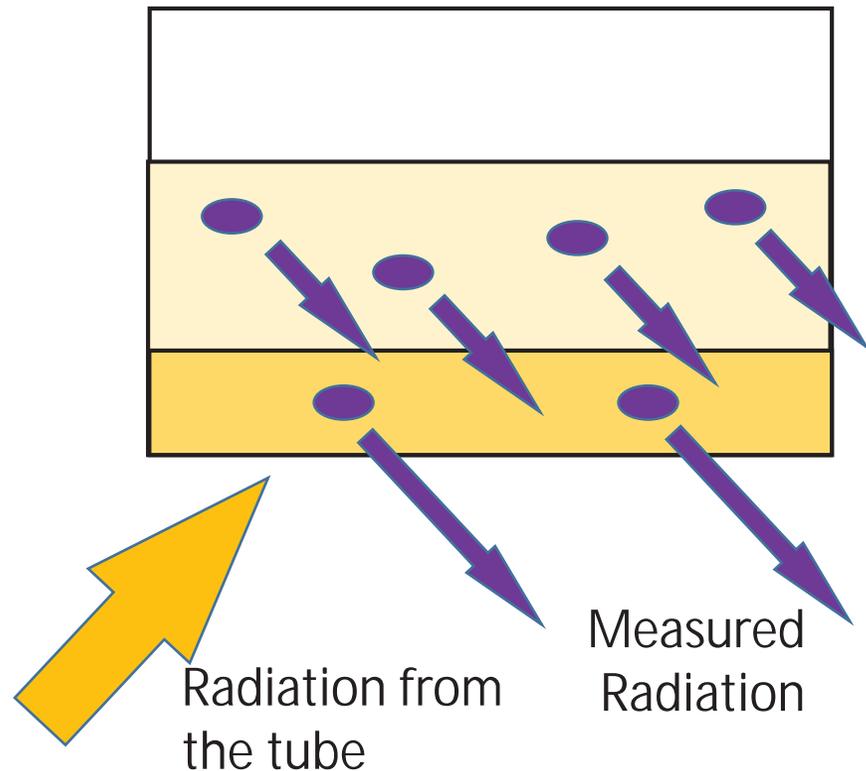

Relationship between radiation intensity of Fe and weight fraction of Fe:

Curve A – negligible matrix effects
Curve B – FeCr,
Curve C – FeNi,
Curve D – FeMn

Fig. 2: Rafał Sitko and Beata Zawisza (2012). Quantification in X-Ray Fluorescence Spectrometry, X-Ray Spectroscopy, Dr. Shatendra K Sharma (Ed.),

From: V. Thomsen (2007) "Basic Fundamental Parameters in X-Ray Fluorescence" Spectroscopy Spectroscopy Magazine May 2007

Remember - XRF is a surface sensitive analytical technique

- No excitation within the upper part of the samples(white)

- Central portion of the sample will be excited by the emitted radiation will be absorbed within the sample (light yellow)

- The measured radiation comes from the surface layers (yellow)

- This 'escape potential' can be measured based on mass attenuation coefficient

$$\frac{\ln(I_0/I)}{u/p \text{ x density}}$$

Radiation from the tube

Measured Radiation

Escape Potential in Different Matrices
(dependent on density)

Line	Energy	Graphite	Glass	Iron	Lead
Cd KA1	23.17 keV	14.46 cm	8.20 mm	0.70 mm	77.30 μm
Mo KA1	17.48	6.06	3.60	0.31	36.70
Cu KA1	8.05	5.51 mm	0.38	36.40 μm	20.00
Ni KA1	7.48	4.39	0.31	29.80	16.60
Fe KA1	6.40	2.72	0.20	* 164.00	11.10
Cr KA1	5.41	1.62	0.12	104.00	7.23
S KA1	2.31	116..0 μm	14.80 μm	10.10	4.83
Mg KA1	1.25	20.00	7.08	1.92	1.13
F KA1	0.68	3.70	1.71	0.36	0.26
N KA1	0.39	0.83	1.11	0.08	0.07
C KA1	0.28	* 13.60	0.42	0.03	0.03
B KA1	0.18	4.19	0.13	0.01	0.01

Approx. Density: ~2.09–2.23 g/cm^3 ~2.5 g/cm^3 ~7.874 g/cm^3 ~11.34 g/cm^3

Photon Escape Potential for Ceramics

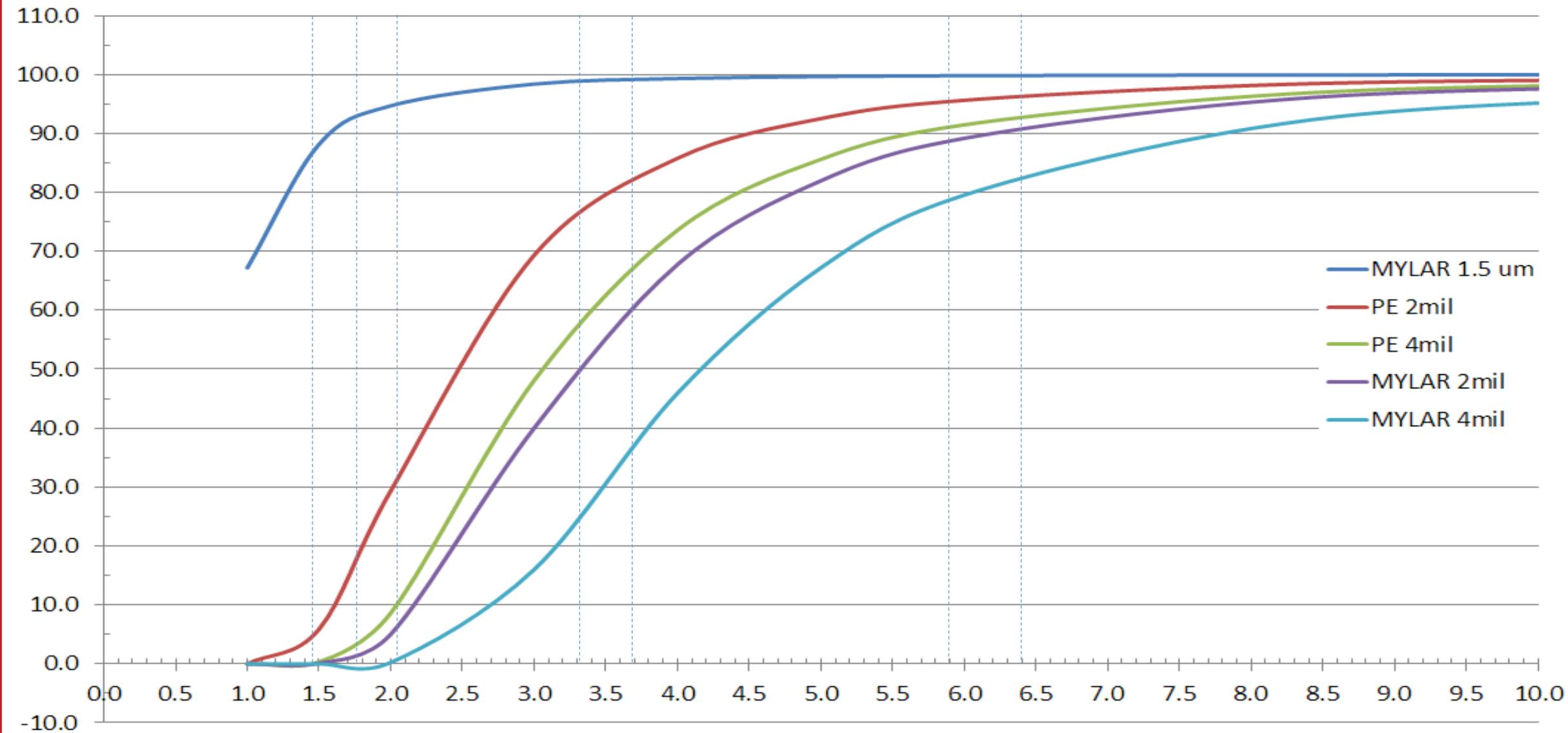| ELEMENT	PHOTON ESCAPE DEPTH	UNIT
Si	24	μm
Ca	70	μm
Fe	271	μm
Rb	0.19	cm
Sr	0.27	cm
Y	0.3	cm
Zr	0.38	cm

Table 3: Approximate photon escape potential for several elements of interest (based on a density of 2.3 g/cm^3). Note that the higher atomic number elements have the potential to escape from a much larger volume of ceramic.

Shugar, A.N. "X-Ray Fluorescence Analysis of HM 1953" Chapter 9 in Real Fake: The Story of a Zapotec Urn. Edited by Justin Jennings and Adam T. Sellen. ROM Publications, Toronto. Pg. 176-189

Attenuation of Mylar and Polyethylene based on polymer thickness for low Z elements

Density (g/cm³): Mylar = 1.4, Polyethylene = 0.93

Sample size and curvature

x 1E3 Pulses

20 kV, 15 μA, vacuum, 180 s

—— Pressed kaolin pellet face   —— Pressed kaolin pellet edge

Ø=13 mm

Si
Al
K
Rh
Ca
Ti
Fe

- keV -
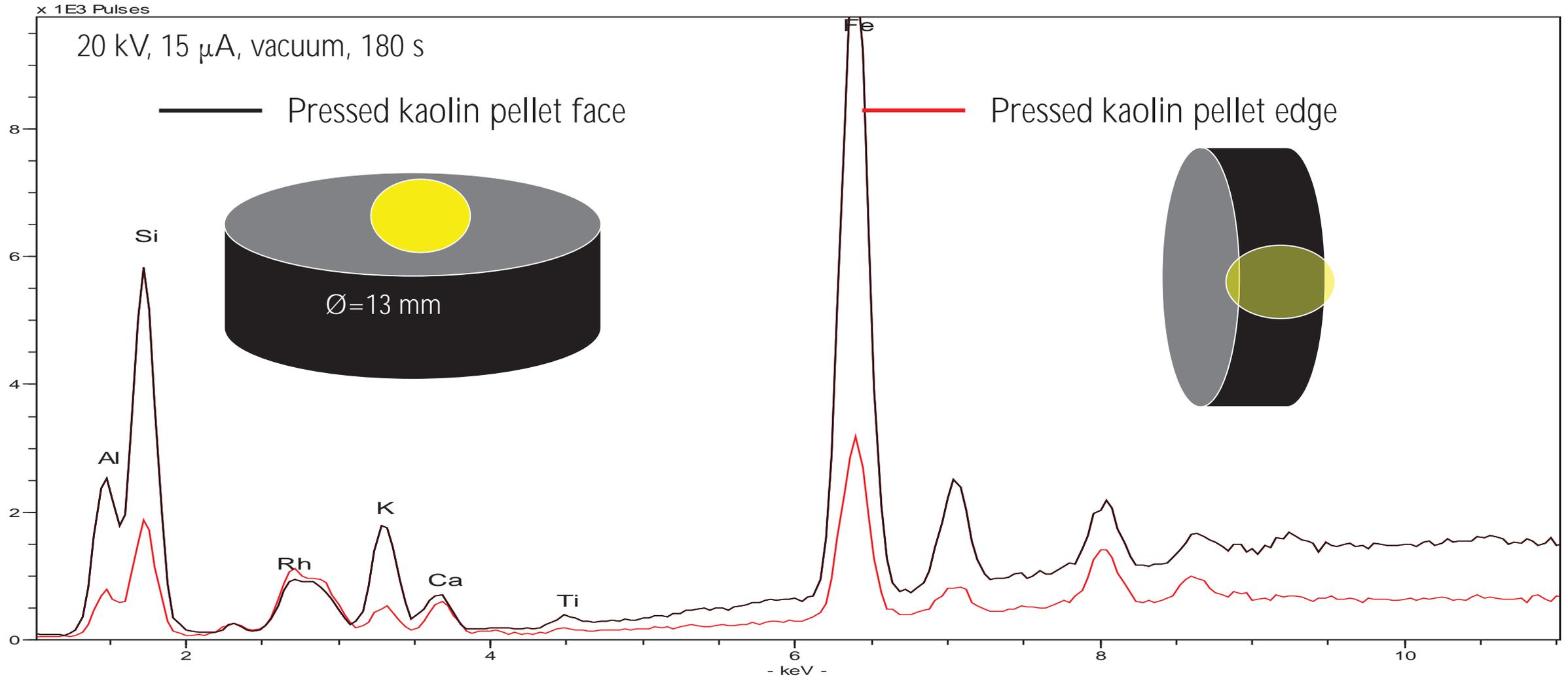
Effect on spectrum with change in sample size and curvature.

A. Bezur, F. Casadio. "The analysis of porcelain using handheld and portable x-ray fluorescence spectrometers". *In Handheld XRF in the Art and Archaeology*
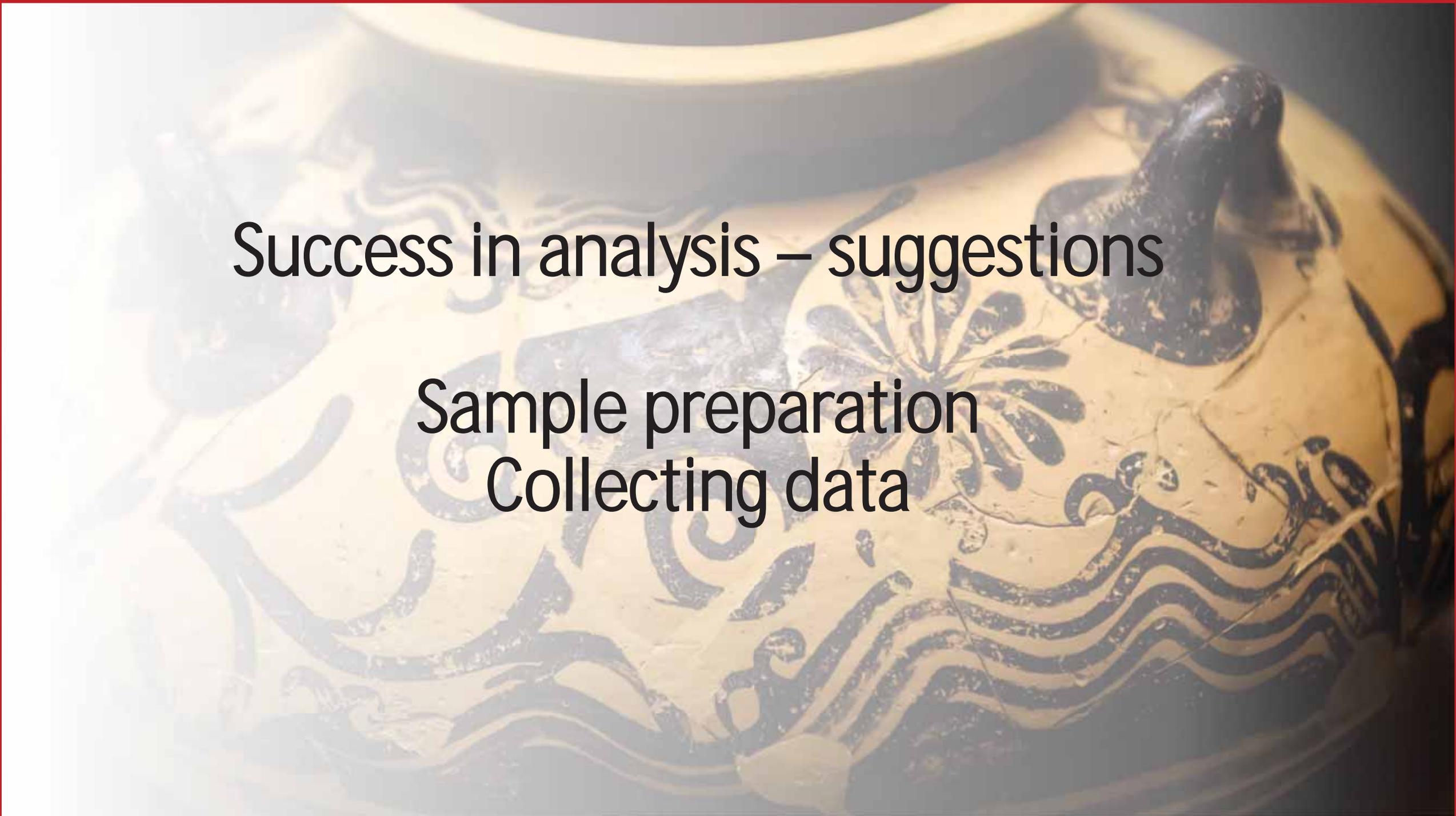
Success in analysis – suggestions

Sample preparation
Collecting data

Options for Ideal Sample and Reference Material Preparation

- Sample should be ground to uniform particle size
- Ideally the particle size should be much smaller than the analyzed layer depth

h = analyzed layer

Tube radiation

Characteristic radiation

Tube radiation

Characteristic radiation
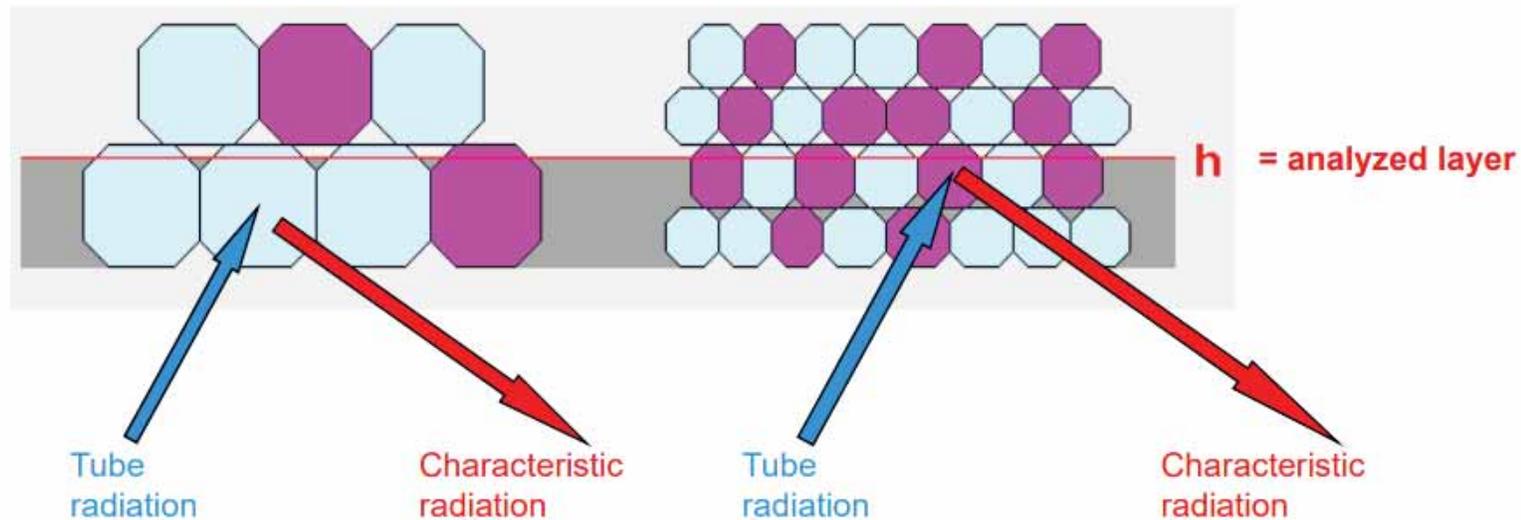
- Powdering, Pressing and Fusing are all options.

Rocks, minerals, ores, ceramics,...

Crushing, pulverizeing

Pouring   Pressing   Fusing

Anzelmo, Bouchard, and Provencher (2014) X-ray Fluorescence Spectroscopy, Part II: Sample Preparation Spectroscopy Volume 29, Issue 7

Sample preparation to improve homogeneity

- Each has benefits and disadvantages.
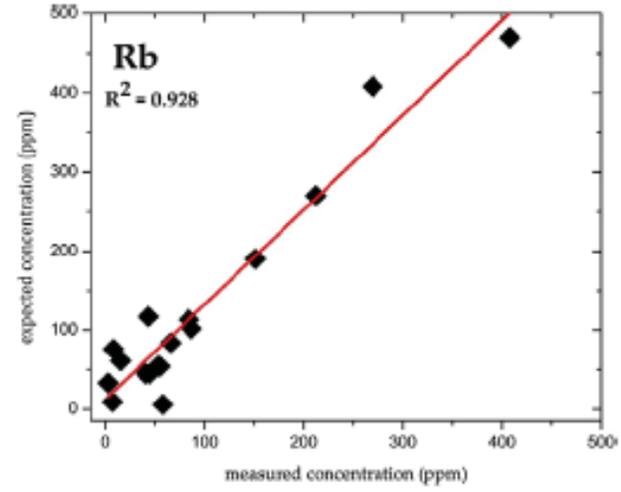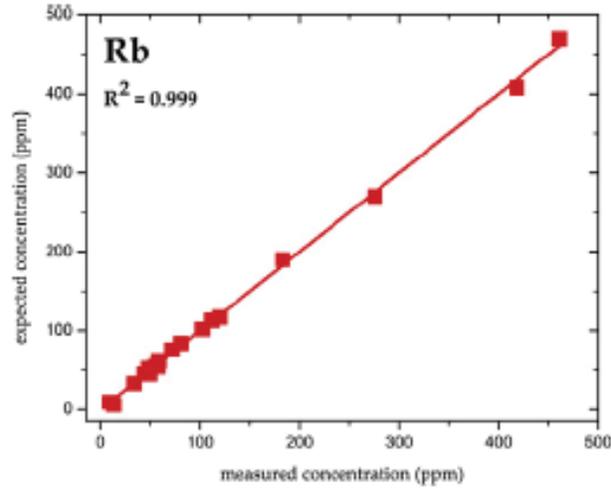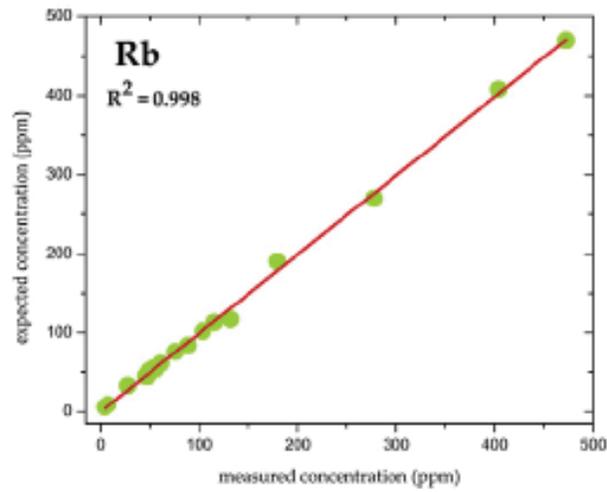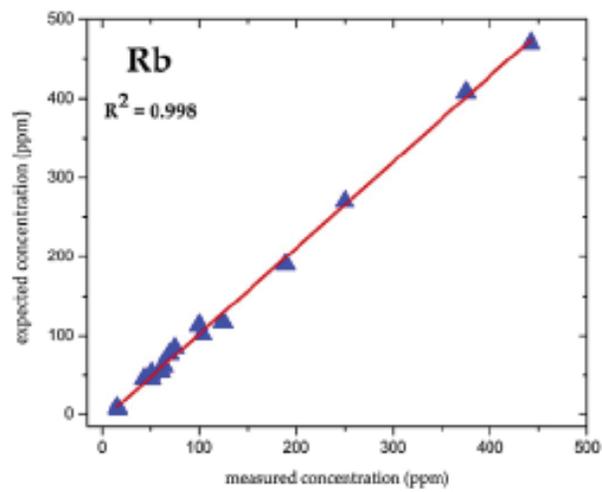- Maintaining consistency in your methodology is key to success.

Powdered samples

Pressed pellets

Borax glass beads / Fusion

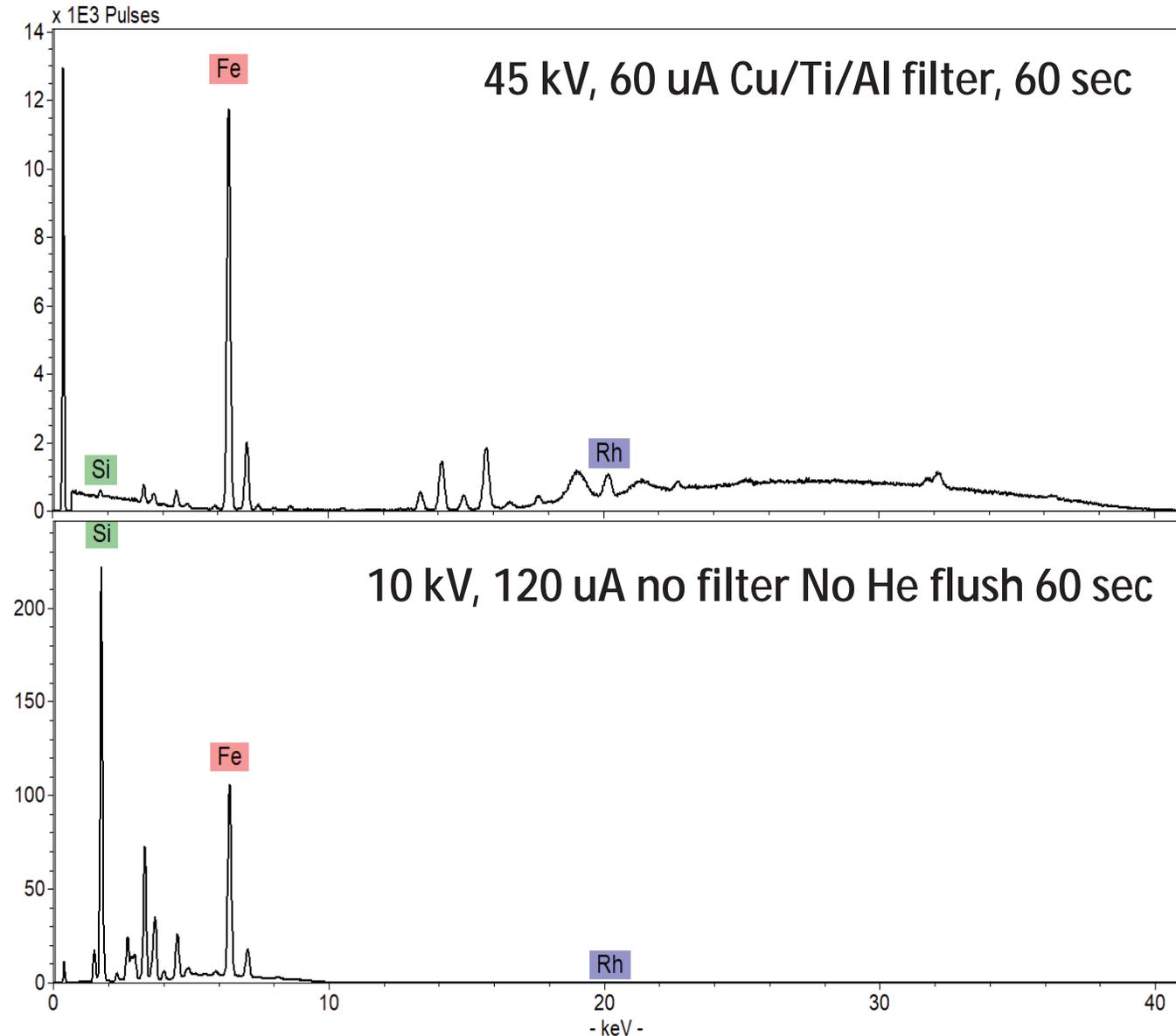# Comparison of WD-XRF, ED-XRF, pXRF-author built Pressed Pellet Cal, pXRF- Bruker mudrock general cal
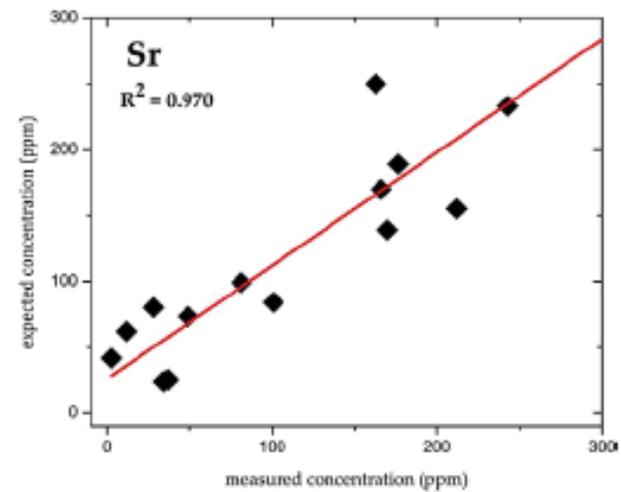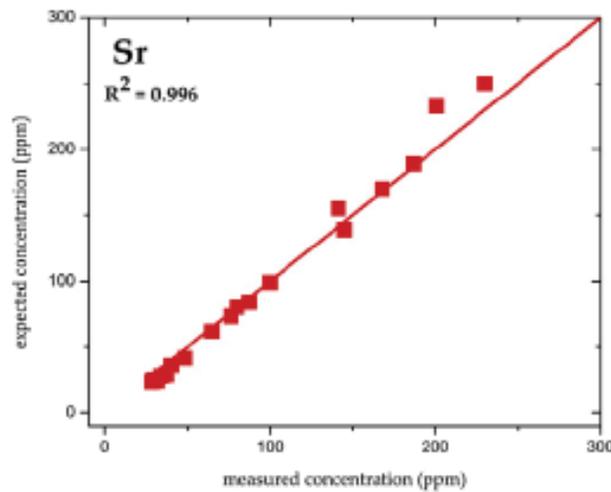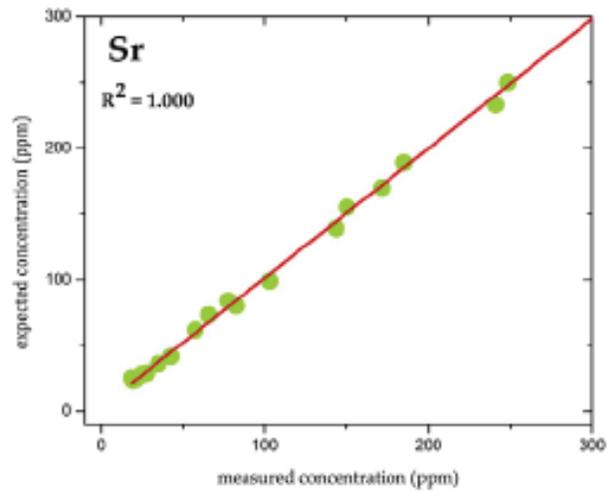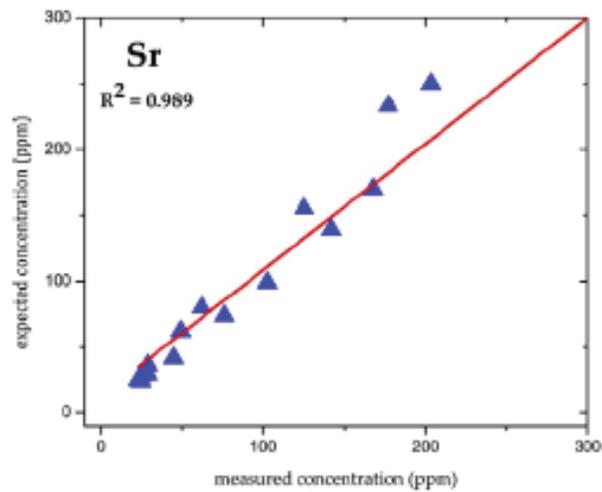
Suggestions for Success – Collecting Data

- Take advantage of X-ray Physics – Change your instrument setting (kV, current, filters, time, and atmosphere) to enhance your data collection.

- Low Z elements – long count times, low kV, relatively high current, He flow, no filter.

- Mid – high Z elements – long count times, high kV, relatively high current, no He, optimal filter.

Table 4

Analytical protocols used to evaluated performance of clay/sediment and 'mudrock' PXRF calibrations.

	CAIS Clay/Sediment calibration	Bruker mudrock calibration
Low Z elements	200 s count time	180 s count time
	15 kV/20 µA	15 kV/20 µA
	He flow	Vacuum
	No filter	No filter
Mid Z elements	200 s count time	60 s count time
	40 kV/30 µA	40 kV/30 µA
	'green' filter:	'yellow' filter:
	300 µm Al/20 µm Ti/150 µm Cu	300 µm Al/20 µm Ti

45 kV, 60 uA Cu/Ti/Al filter, 60 sec

10 kV, 120 uA no filter No He flush 60 sec

Creating a Calibration – Cross Analysis

- In addition to proper sample preparation – obtain quality comparable data
  - NAA and/or ICP-MS can provide reliable compositional data to build a cross reference set.
- Retain some samples for a Validation Set to test your calibration
  - Comparing your cal to samples used to build your calibration is NOT recommended.
- Different XRF manufacturers have different options for calibration programs (i.e. Easycal – Bruker), or use a self standing software (i.e. Cloudcal - v3.0 Drake, B.L. 2018. CloudCal v3.0. GitHub. https://github.com/leedrake5/CloudCal. doi: 10.5281/zenodo.2596154)
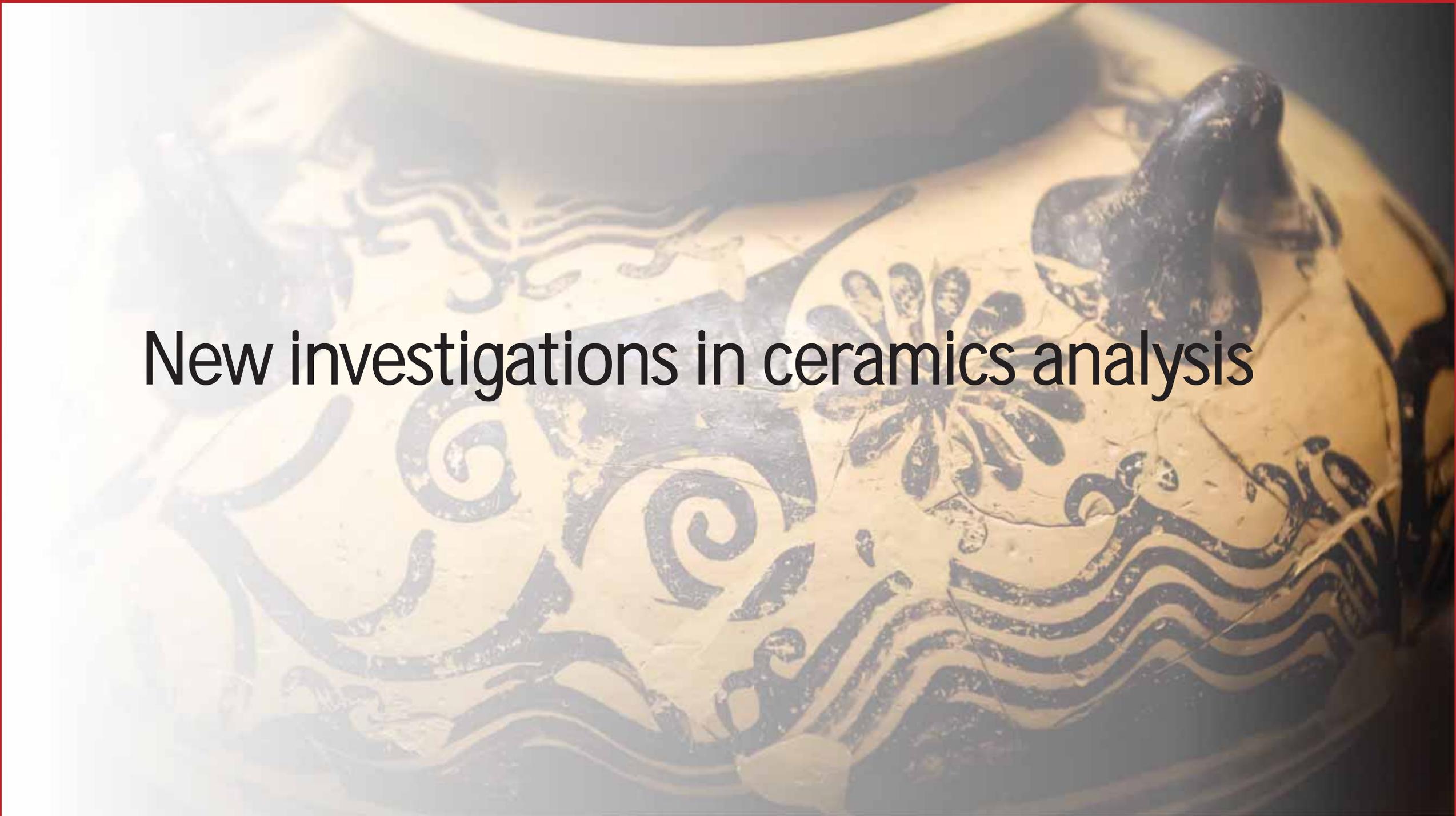
New investigations in ceramics analysis

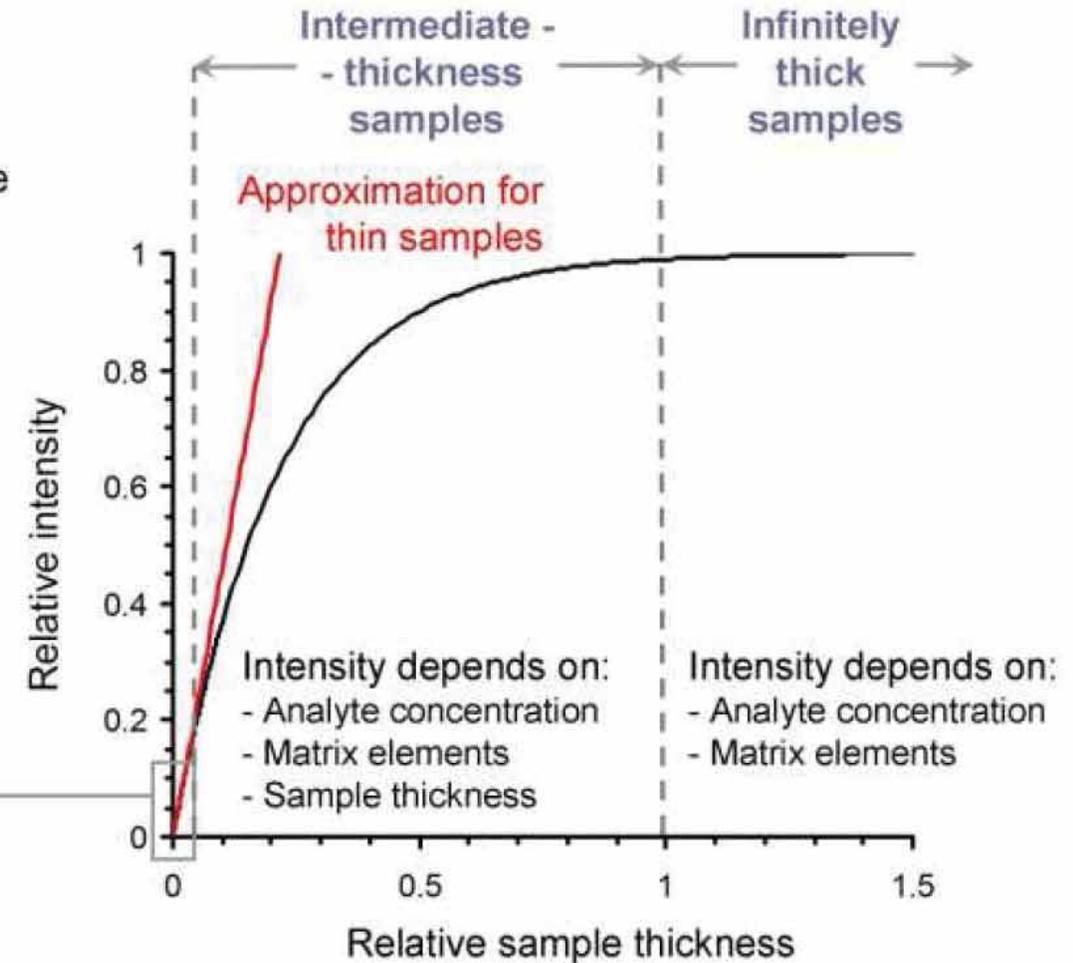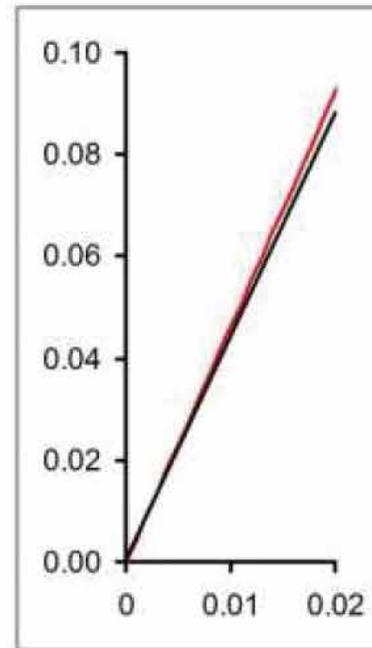# Scientific investigation of ceramics materials from Honduras

- Aim – investigate creating two different calibration models
 - Sanded flat and cleaned fragments.
  - Thin films

Rafał Sitko and Beata Zawisza Quantification in X-Ray Fluorescence Spectrometry
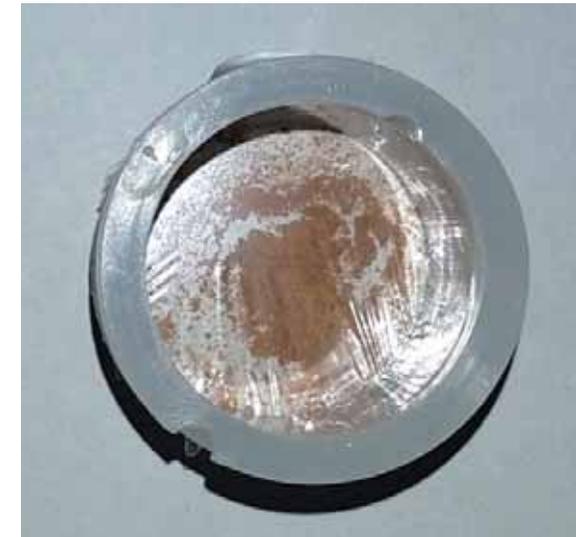
Scientific investigation of ceramics materials from Honduras

(Shugar, Schortman and Urban, NSF award # 1733890)

- 430 samples from archaeological context in Honduras

- Preparation
  - Sanded flat (both sides) and cleaned fragments.
  - Thin films of 0.02 grams from drilled cores.

- Analysis
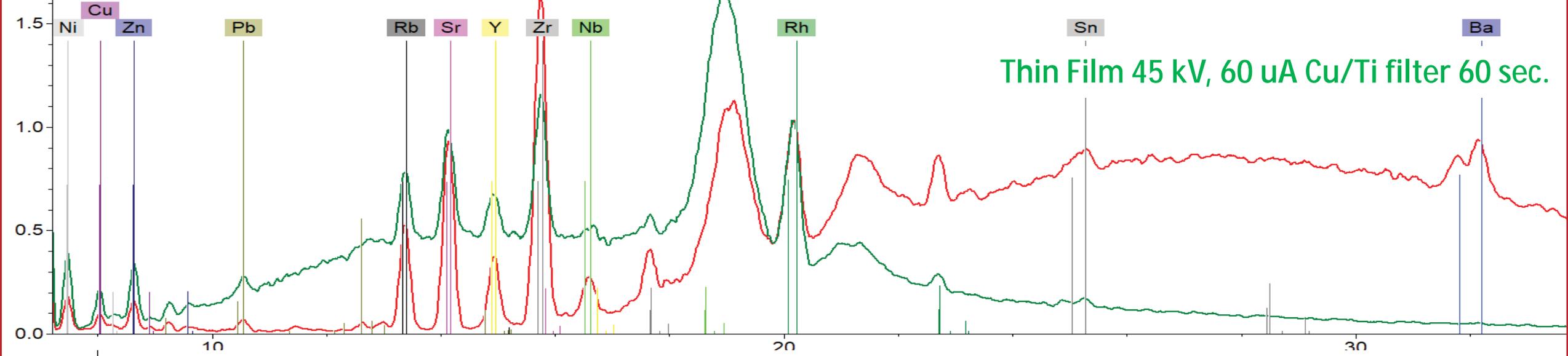 - Using empirical calibrations and new theoretical ones
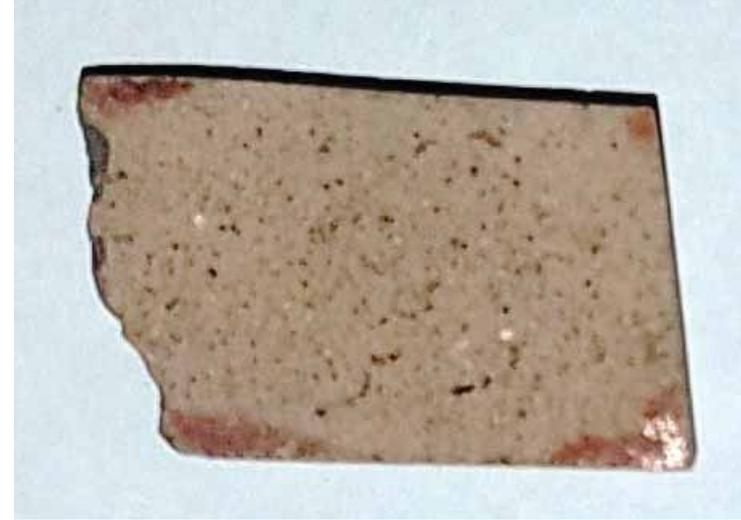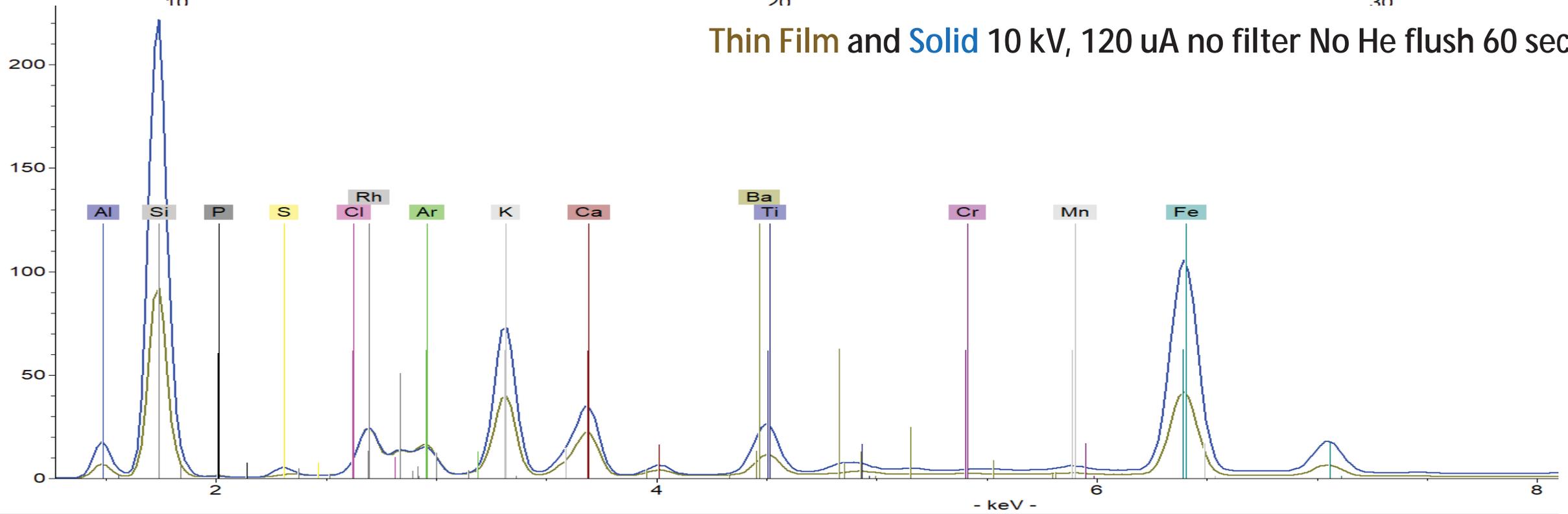

Sanded and cleaned

Drilled and thin filmed

Solid 45 kV, 60 uA Cu/Ti/Al filter 60 sec.

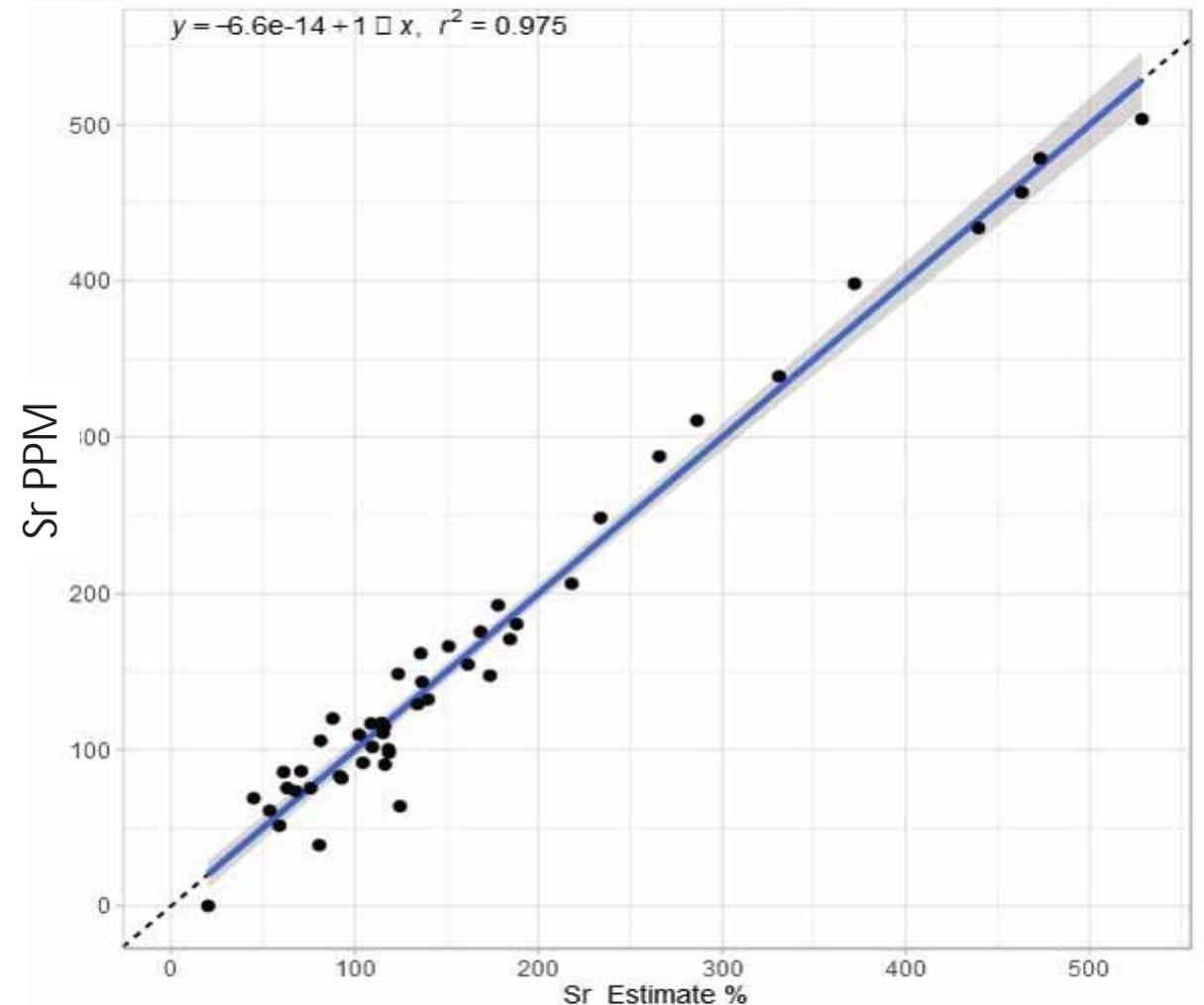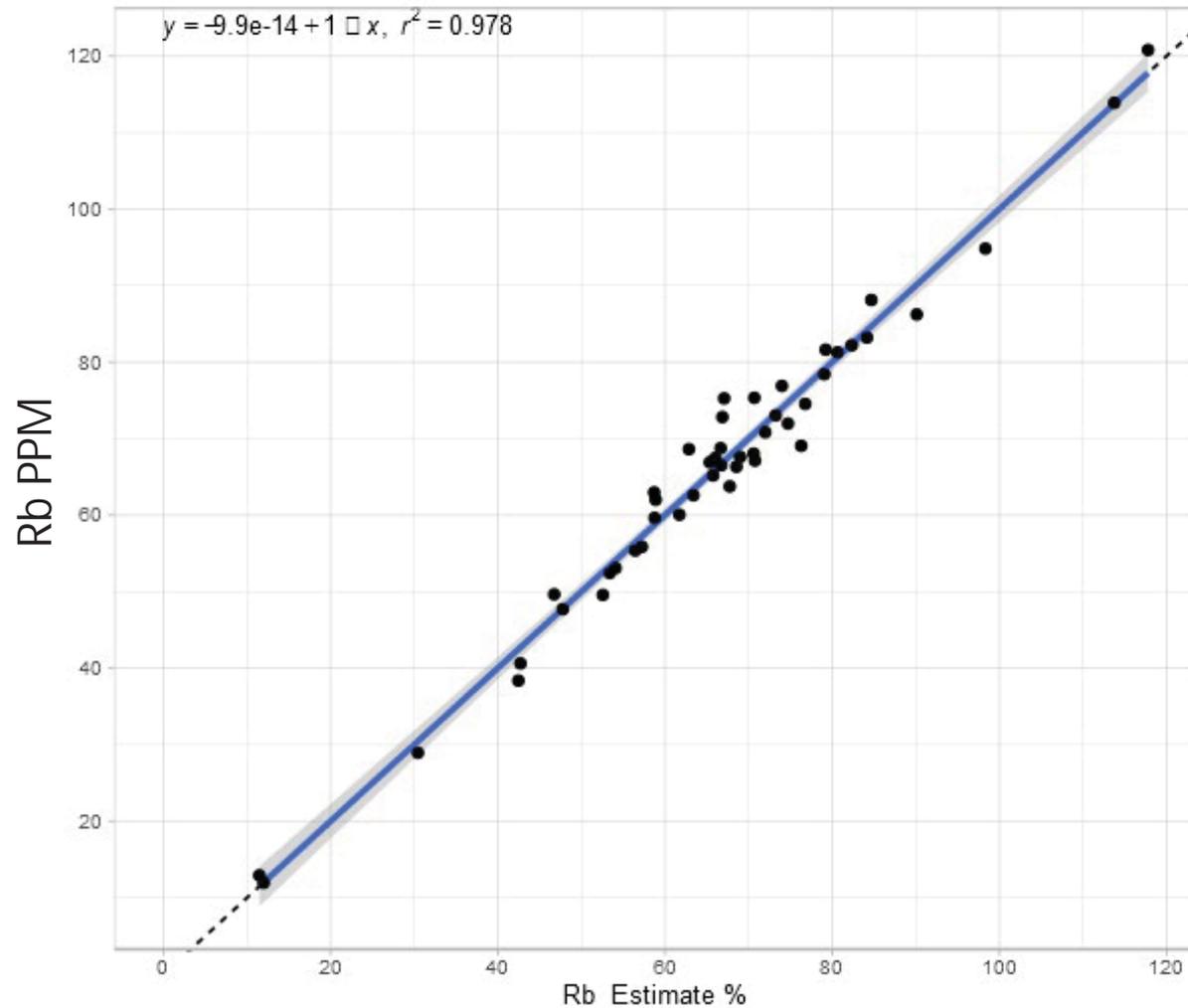Thin Film 45 kV, 60 uA Cu/Ti filter 60 sec.

Thin Film and Solid 10 kV, 120 uA no filter No He flush 60 sec.

Preliminary Results

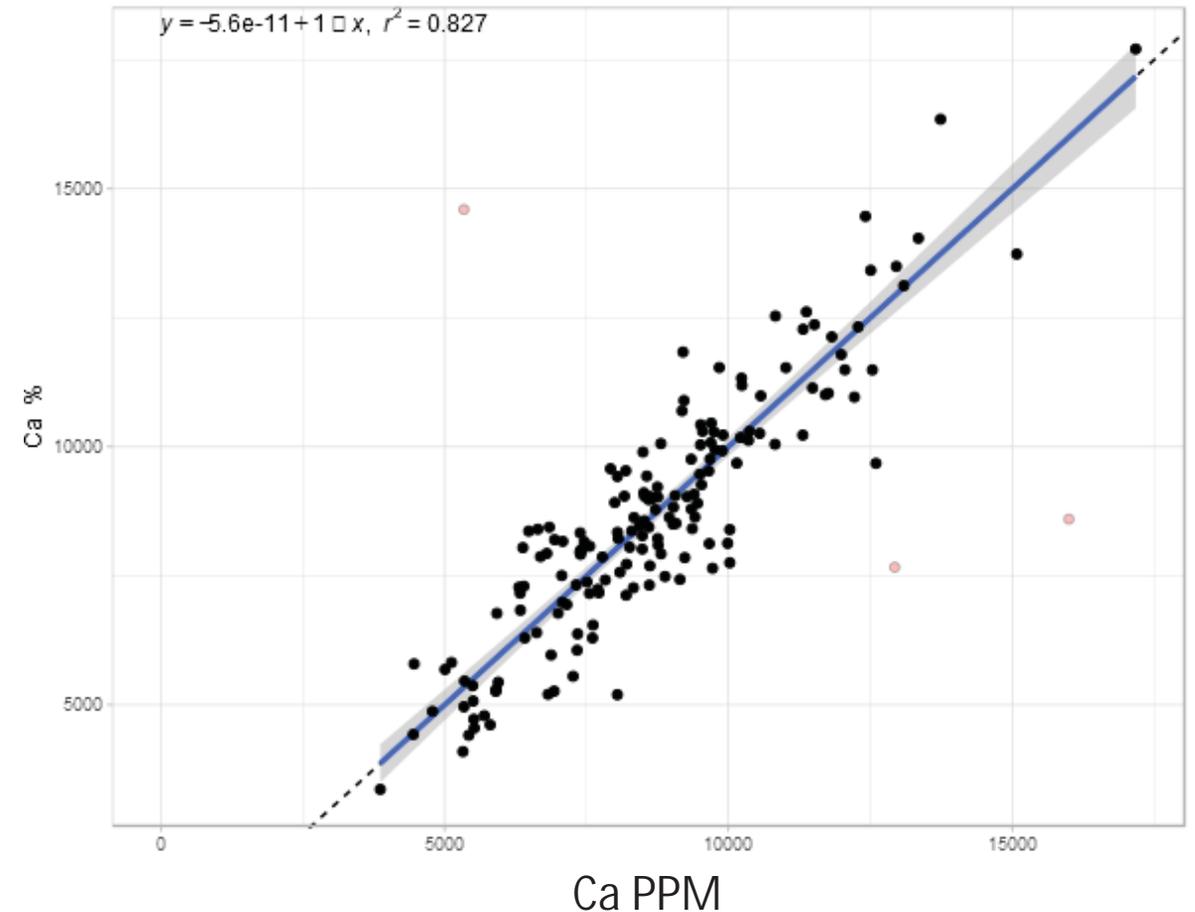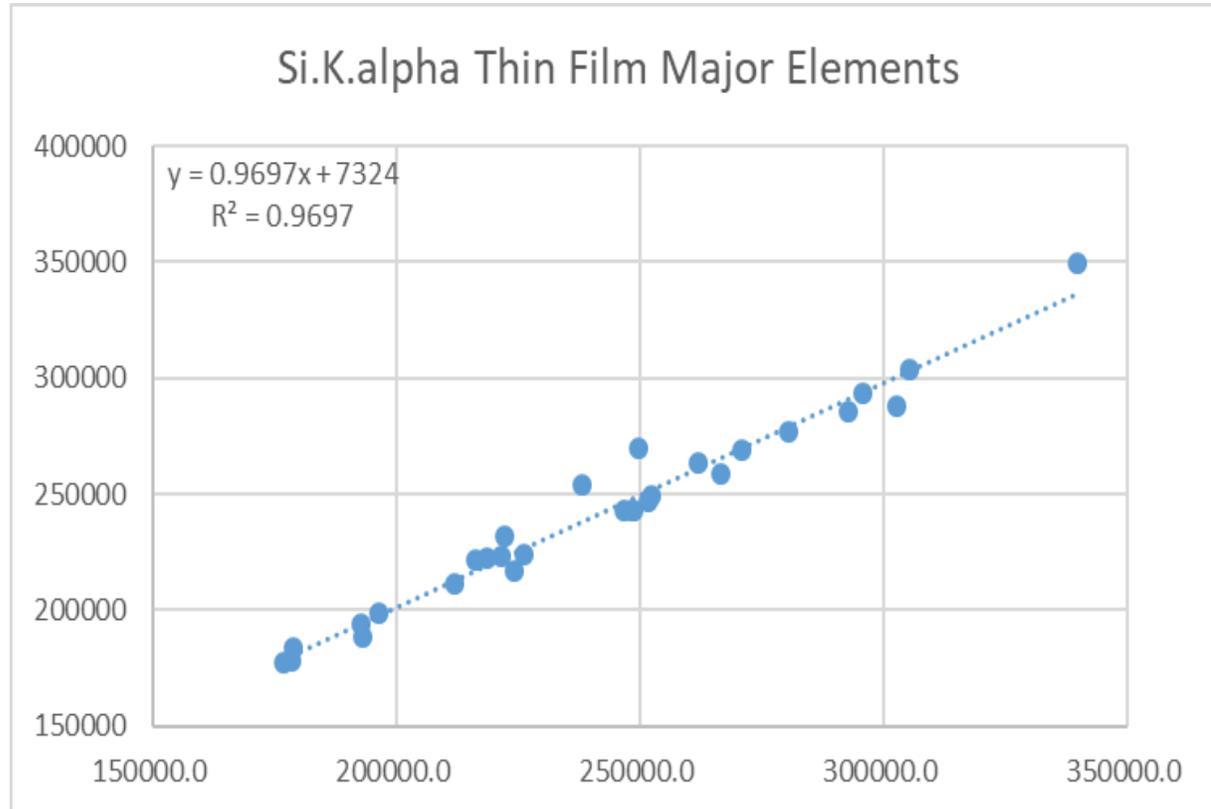- Solid samples trace element calibration curves for Rb and Sr
  - Lucas-Tooth Calibration with total counts normalization

Preliminary Results

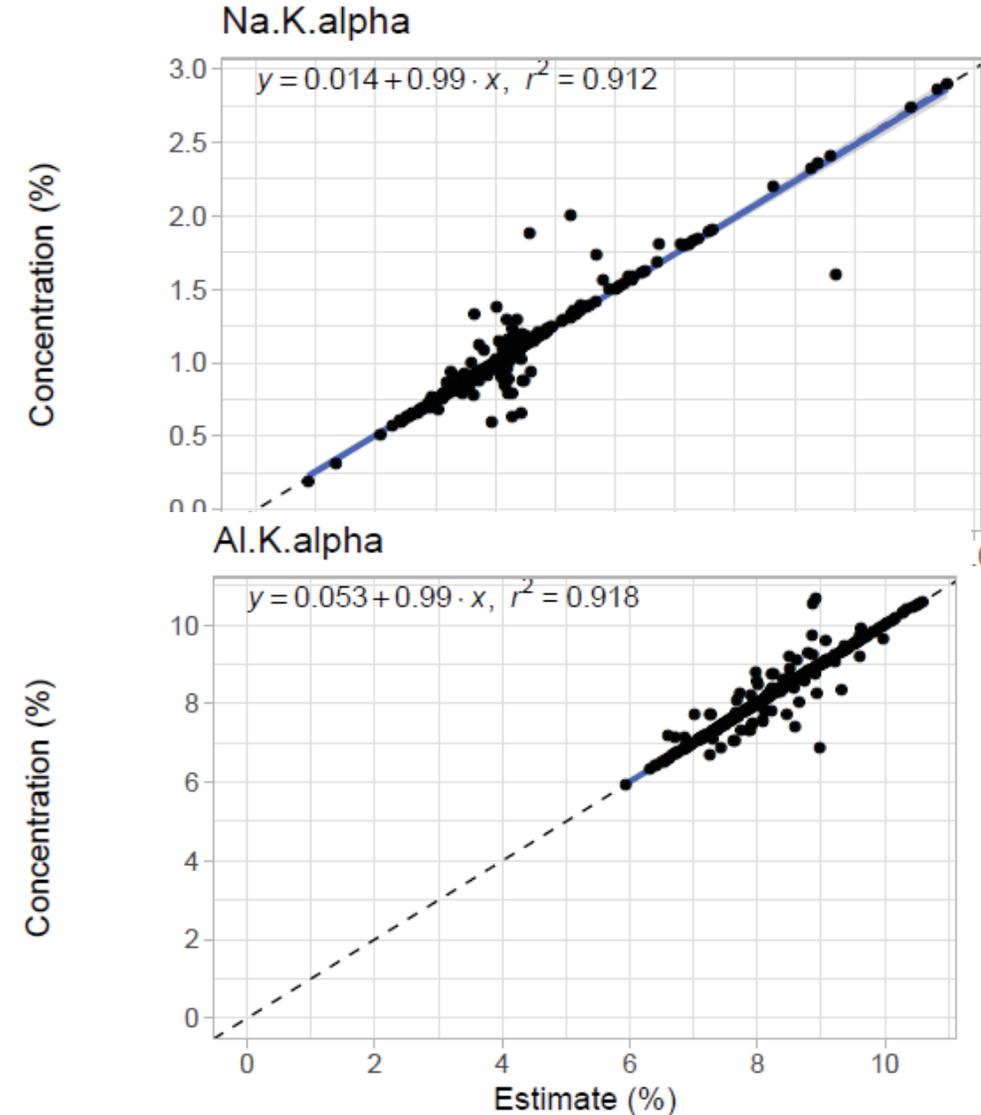- Thin Film samples Major elements calibration curves for Si and Ca
  - Lucas-Tooth Calibration with time normalization

Si.K.alpha Thin Film Major Elements

$y = 0.9697x + 7324$
$R^2 = 0.9697$

$y = -5.6e{-}11 + 1 \square x, \ r^2 = 0.827$

Ca %

Ca PPM

Newer Machine learning algorithms

- Forest algorithm
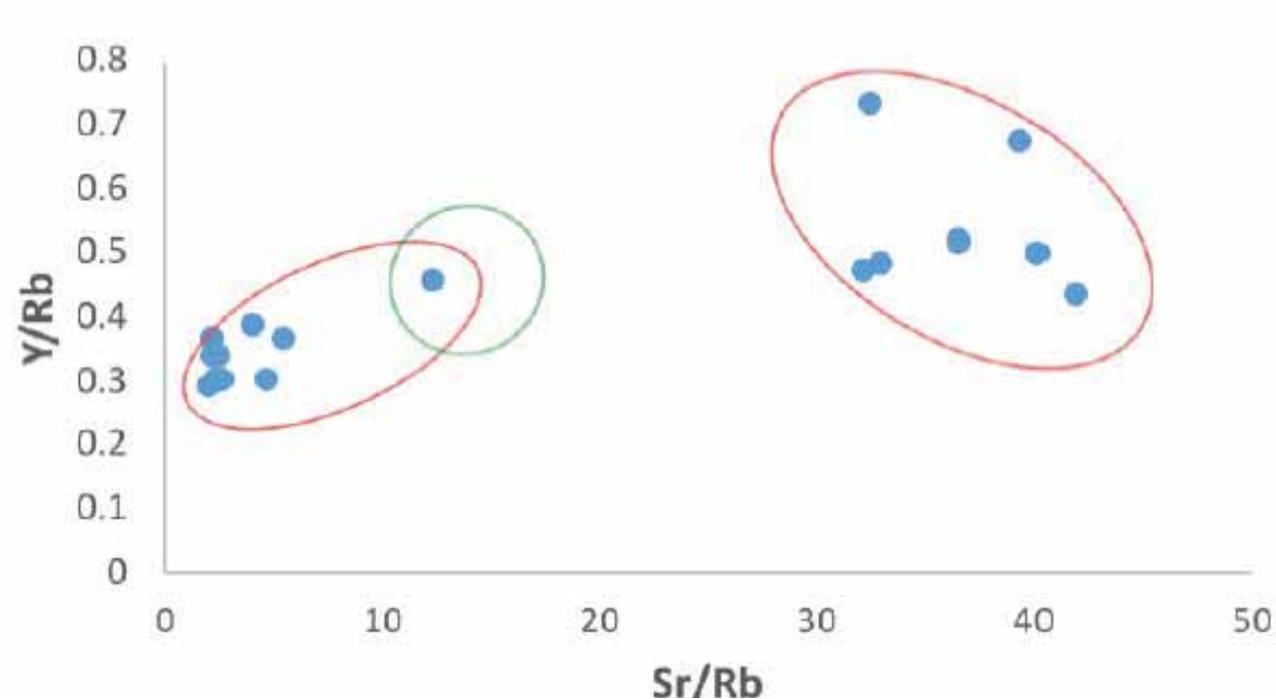- Neural Networks
- XGBoost

- Rahman, Ashfaqur, et al. "A machine learning approach to find association between imaging features and XRF signatures of rocks in underground mines." *2015 IEEE SENSORS*. IEEE, 2015.

- Radtke, Martin. "Machine learning for direct quantification of XRF measurements." (2019).

- Heginbotham, Arlen, Robert Erdmann, and Lee-Ann C. Hayek. "The dating of French gilt bronzes with ED-XRF analysis and machine learning." *Journal of the American Institute for Conservation* 57.4 (2018): 149-168.

Na.K.alpha

$y = 0.014 + 0.99 \cdot x,\ r^2 = 0.912$

Concentration (%)

Al.K.alpha

$y = 0.053 + 0.99 \cdot x,\ r^2 = 0.918$

Concentration (%)

Estimate (%)

XGBoost calibration curve for ceramics solid trace scan for Na and Al – courtesy of Lee Drake

Potentially accept qualitative data comparison

- Faster results – reduced cost – can always apply calibration in the future
- Look at the area under peak for elements of interest.
- In many cases, grouping can be extracted.

Area under peak elemental ratios to define ceramic grouping

Shugar, A.N. "X-Ray Fluorescence Analysis of HM 1953" Chapter 9 in Real Fake: The Story of a Zapotec Urn. Edited by Justin Jennings and Adam T. Sellen. ROM Publications, Toronto. Pg. 176-189

Summary

- Come prepared –
  - Know what your samples is composed of
  - If you need quantification –
    - you must create reference materials that fully resemble your unknowns
    - Cross analyze your unknowns using a different technique (i.e. ICP)
    - Be ready to properly prepare your samples
    - Reduce the variables
  - Be prepared to accept qualitative data
    - Ideal for survey of large assemblages

- The Future is bright!
  - The development of XRF is continuing
  - Newer technologies are pushing the boundaries of what is possible
  - Development of new algorithms is making calibration of complex systems easier

New Tracer 5g – Graphene window on detector allows for the identification of F