

Basics of X-ray Fluorescence Spectrometry

Overview

- Geochemical methods used in the geo- and environmental sciences
 - How XRF compares with other common analytical methods
- Generation of x-rays
- XRF spectrometer fundamentals
 - WDXRF
 - EDXRF
 - TXRF
- Spectral characteristics
 - continuum
 - kV, mA, Z, excitation potential
 - Rayleigh & Compton scatter
 - sum peaks
 - Escape peaks
 - Low energy shelves
 - Line overlaps
- Examples of spectra
- Which method and machine is for you?

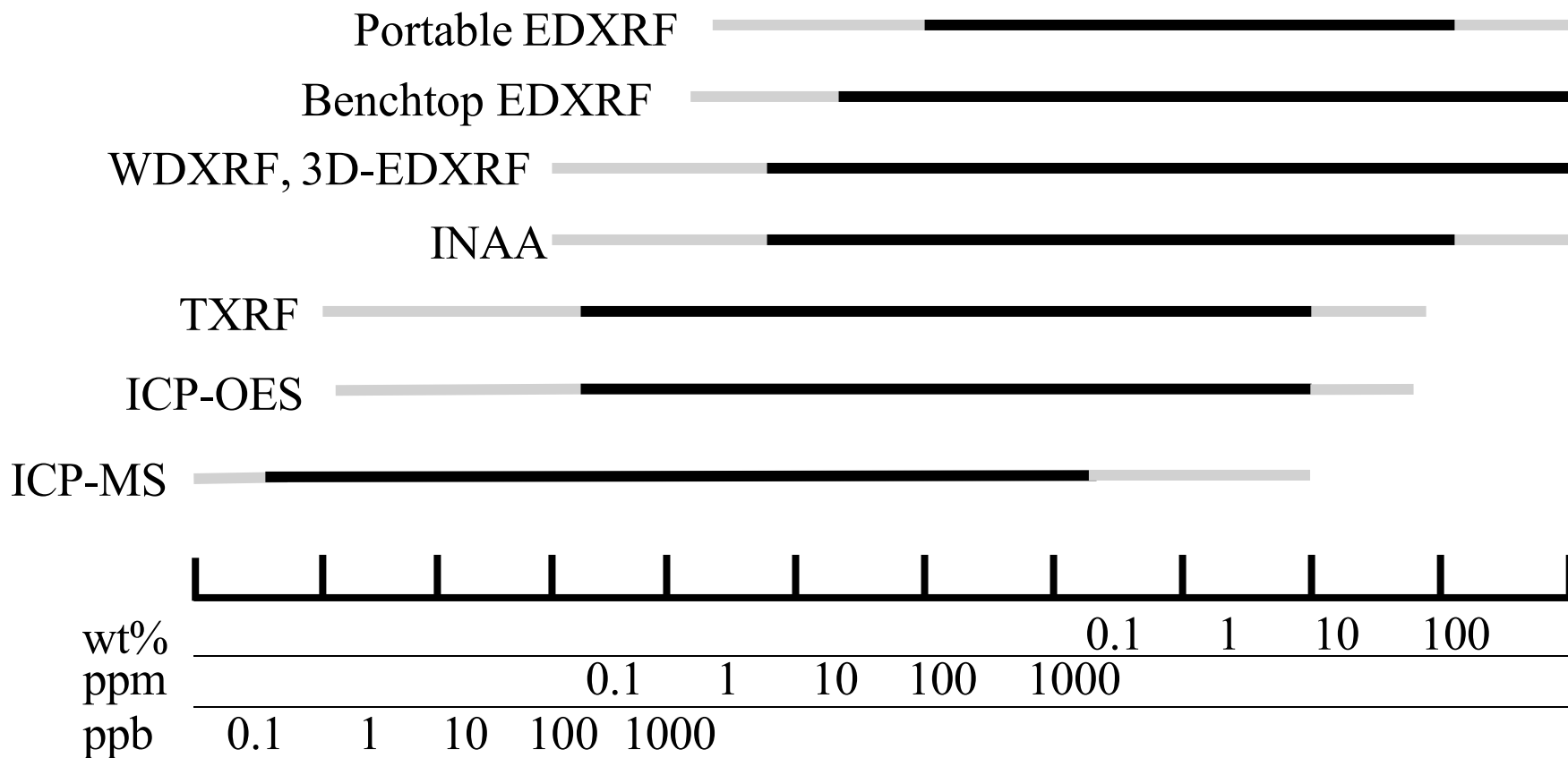
Geochemical methods

- Inductively Coupled Plasma
 - ICP-OES
 - ICP-MS
- Instrumental Neutron Activation Analysis
- X-ray Fluorescence Spectrometry
 - Fluorescence
 - Wavelength Dispersive XRF
 - Energy Dispersive XRF - Portable, Transportable (Benchtop), 3D geometry
 - Total Reflection XRF

Typical analytical ranges

Key for a typical Row 4 element, light matrix

Measured readily
Measured with difficulty



Some typical spectrometers

	Bruker AXS	Innov'X	Microanalytik
Portable			
Transportable			
Lab scale EDXRF			
WDXRF			

Generation of x-rays

Excitation of atoms by X-ray bombardment

- ejection of inner electrons from an atom by X-rays (from a tube or secondary target)
- this creates electron vacancies

Atom now in excited, unstable state

Generation of x-rays

De-excitation of atoms, by cascade movement of electrons from outer shells to fill electron vacancies in inner shells, leads to emission of X-rays “characteristic” of the source atom.

Atom changes back from excited to ground state, and in the process “secondary” (fluorescent) X-rays are emitted.

Generation of x-ray characteristic lines

Cascade movement of electrons from outer shells to fill electron vacancies in inner shells. All transitions occur simultaneously.

Low-Z elements = low energy (long wavelength) X-rays

High-Z elements = high energy (short wavelength) X-rays

Differences are sufficient to distinguish elements - hence XRF spectrometry

Characteristic intensities of some K_α/K_β & L lines

- Approximate intensities, *between* elements
- The relative intensity of the K_β increases systematically with decreasing atomic number
- L lines show no systematic trend with atomic number

XRF spectrometer fundamentals

WDXRF: the analyzing crystal disperses the x-rays according to their wavelength. The detector is just a simple counter.



EDXRF: the detector discriminates the x-rays according to their energy.

(C) Total Reflection XRF

TXRF: the x-ray beam is reflected from a surface, fluorescing a thin film of sample on a highly polished carrier disc. This results in a very low background and vastly improved detection limits. The detector is energy dispersive.

Spectrometer Resolution

- At low energy (medium-long wavelength; $>\sim 2\text{\AA}$ or $<\sim 6\text{ keV}$), WDXRF is far superior to EDXRF
- At higher energy (shorter wavelength; $<\sim 0.8\text{\AA}$ or $>\sim 16\text{ keV}$), EDXRF is better than WDXRF

Spectral characteristics

- Controls on the continuum
 - voltage
 - current
 - atomic number
 - excitation potential
- Scatter
 - Rayleigh
 - Compton
- Some spectral artefacts
 - sum (& pulse pile-up) peaks
 - escape peaks
 - low energy shelves

X-ray Continuum

The intensity of the X-ray continuum is determined by;

- Voltage on the X-ray tube (kV)
- Current on the X-ray tube (mA)
- Atomic number of the target element (Z)

According to;

Significance of Excitation Potential

The excitation potential is the minimum X-ray tube operating potential (keV) that can excite characteristic lines in the tube target OR in the sample.

Rayleigh & Compton scattering

- Some incident x-ray photons scatter elastically (without loss of energy) from the sample - this is called Rayleigh scattering
- Other x-ray photons collide with loosely bound, outer shell electrons (especially for low atomic number elements e.g. C, N, O), and scatter with a loss of energy (increased wavelength). This is called Compton scatter
- The amount of energy lost depends on the angle of scatter
- This results in a second, broader peak – the Compton peak – on the low energy (long wavelength) side of each Rayleigh peak.

Loss in energy (gain in wavelength)
of the scattered photon
 $\lambda + 0.0243 (1 - \cos\phi)$

Higher
energy

Lower
energy

Sum peaks

- Sum (pulse pile-up) peaks form from the “simultaneous” arrival of two x-ray photons. If the counting circuits can’t discriminate them, then they are counted as a single photon of higher energy.
- This may be two (or more rarely, three) photons of the same element, or photons from different elements.

Si excited by 15 keV electrons. Only a small sum peak is present, with no significant pile-up continuum.

Mn excited by 15 keV electrons, with 2 x and 3 x sum peak and pulse pile-up spectrum.

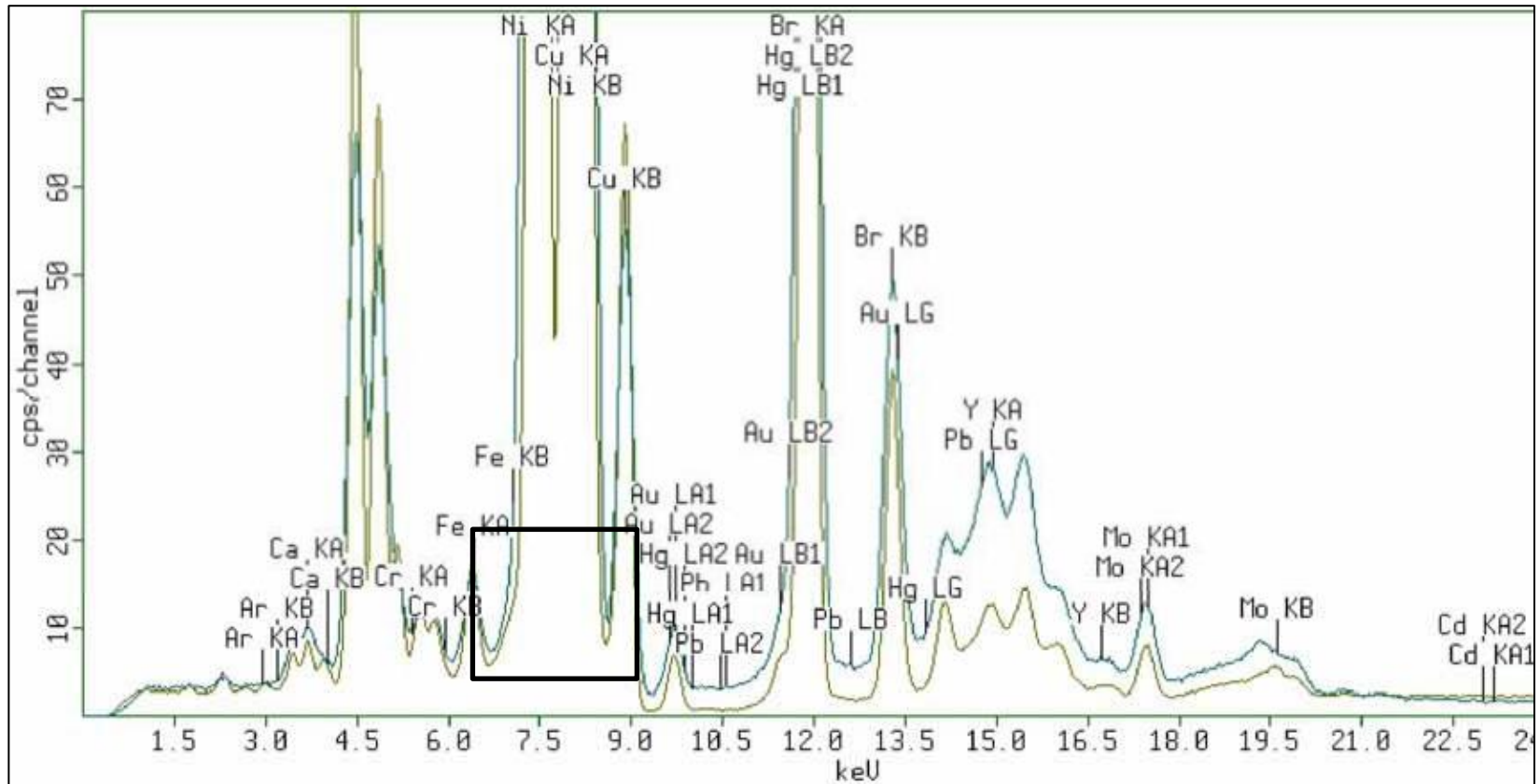
Escape peaks

- Escape peaks form from stimulation of Si in the detector, which fluoresces. Escape peaks form ~ 1.7 keV down-energy of abundant elements in the sample
- Larger escape peaks are produced from spectral lines with energies closer to the SiK absorption edge energy, due to more efficient absorption/enhancement of the Si

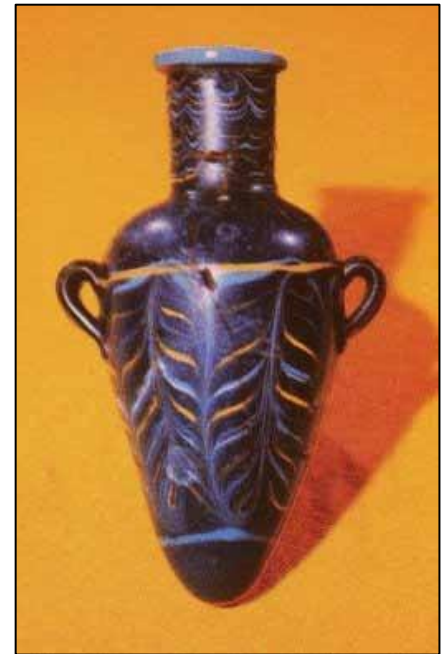
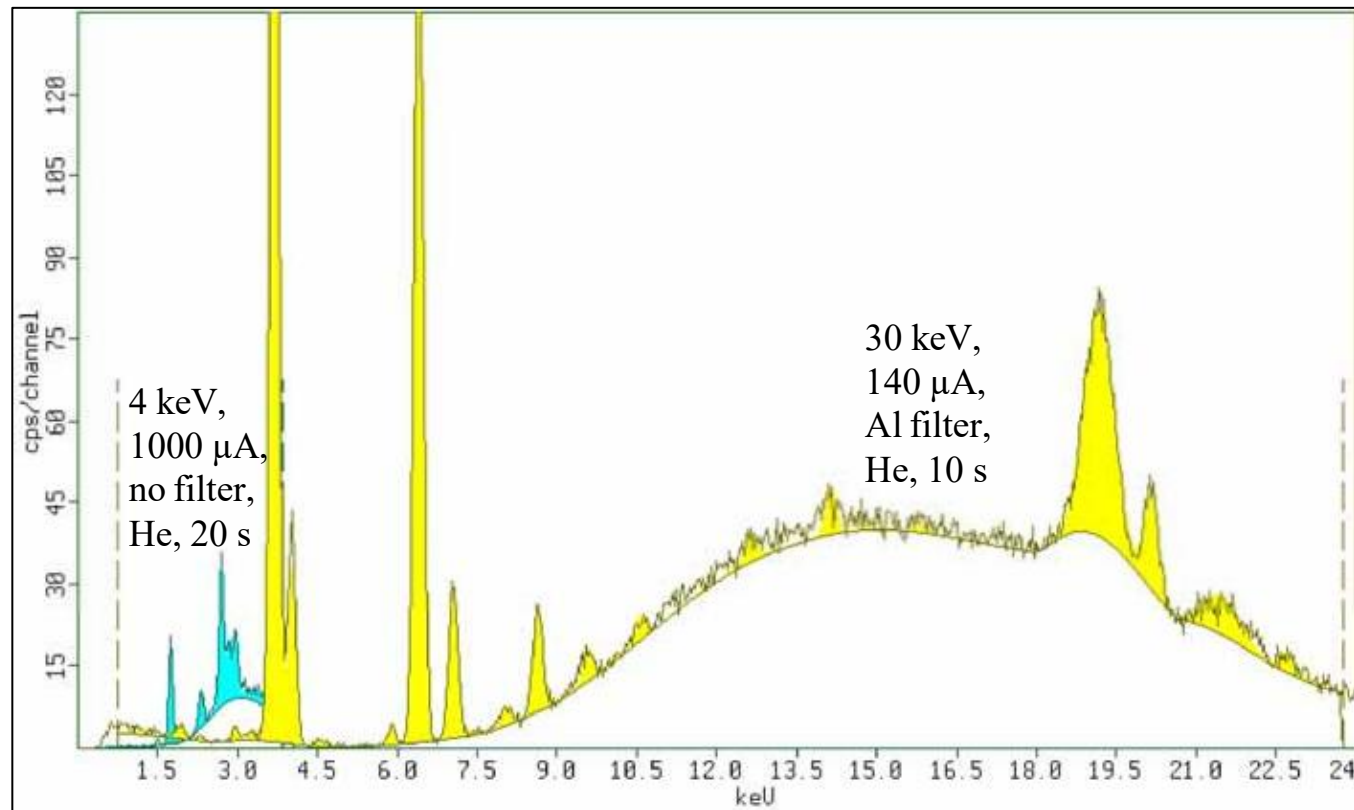
Low energy shelves

- Some detectors allow charge leakage, creating an apparent non-gaussian distribution of x-rays in the spectrum. This is an artefact which is removed in some software but not others.

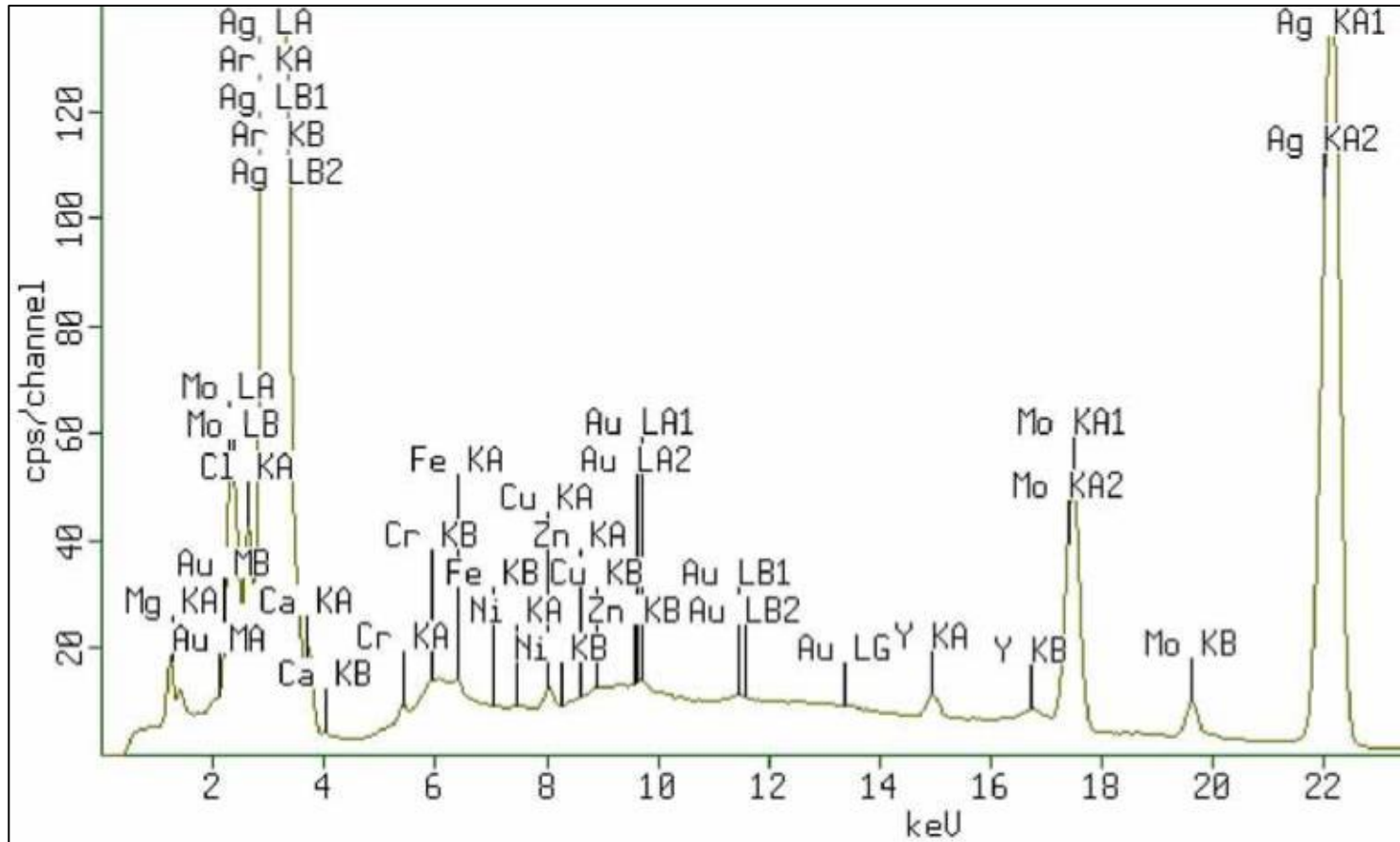
Small peaks can hide under these shoulders and lead to poor deconvolution and enhanced detection limits. This only occurs at around 1-2% of the peak area.



Examples of spectra

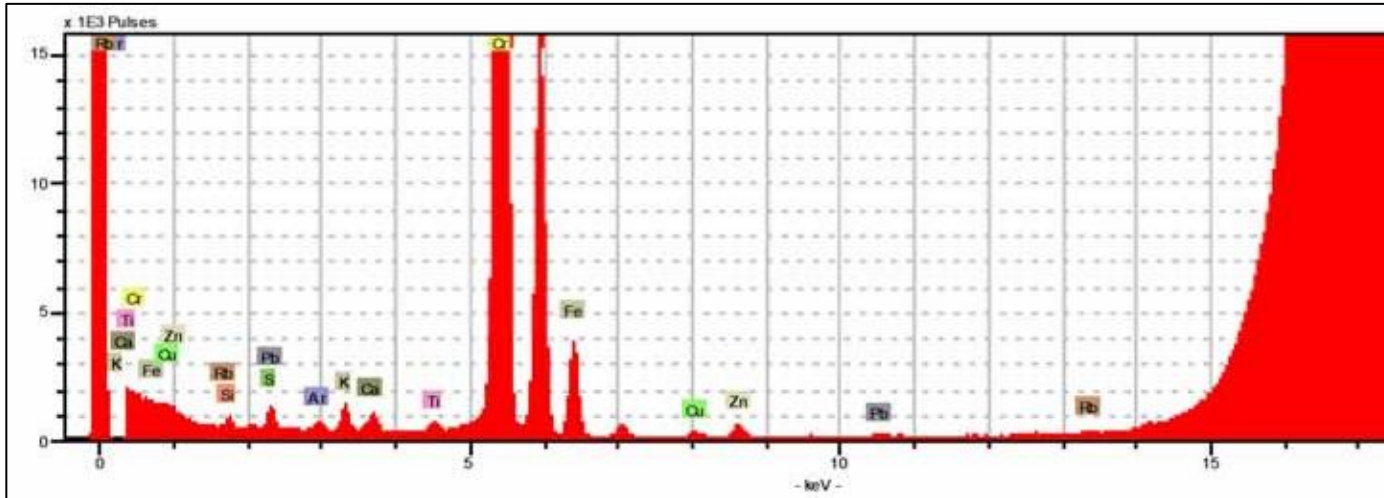


Examples of spectra

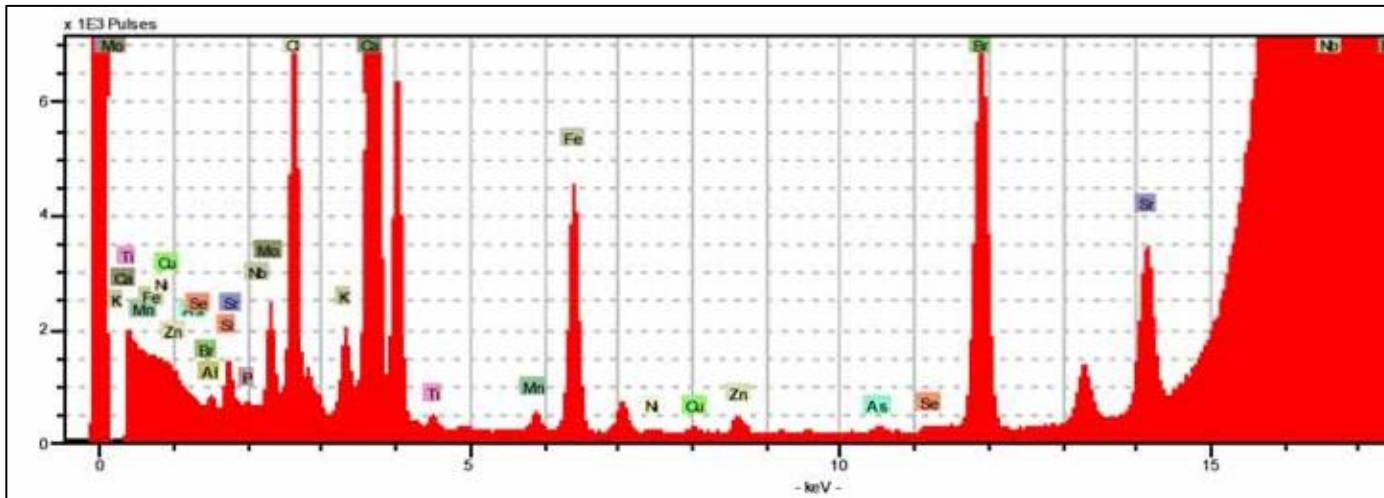


Sterling silver - Mo tube, 30 keV, 20 μ A, no filter, air, 1000 s (measured 99.6% Ag)

Examples of spectra



Felt pen - Bruker Picofox TXRF, Mo tube, 50 keV, 750 μ A, 1000 s, air, no filter.



Antarctic Ascidian (sea squirt) - Bruker Picofox TXRF, Mo tube, 50 keV, 750 μ A, 1000 s, air, no filter

What analytical method should you use?

That depends on your target analytes, Data Quality Objectives and many other factors...

If there was a perfect machine, we'd all have that and nothing else!!

Speed? ←
XRF

Sub-ppm
sensitivity? ←
ICP, TXRF

Complex
matrix? ←
WDXRF?

Low
budget? ←
Trans/portable XRF

→ Small
sample?
ICP, TXRF

→ Sample
throughput?
XRF

→ Few
personnel?
Trans/portable XRF