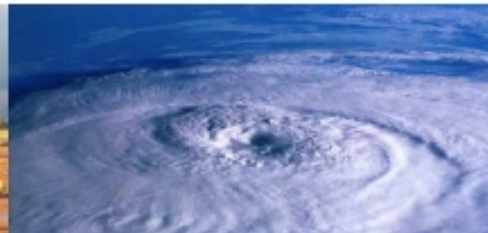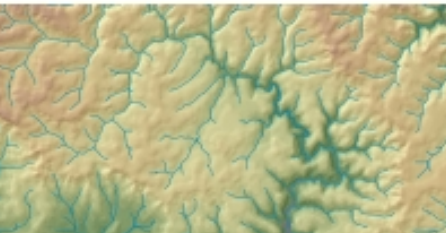# Basics of X-ray Fluorescence Spectrometry

Damian Gore

Macquarie University

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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
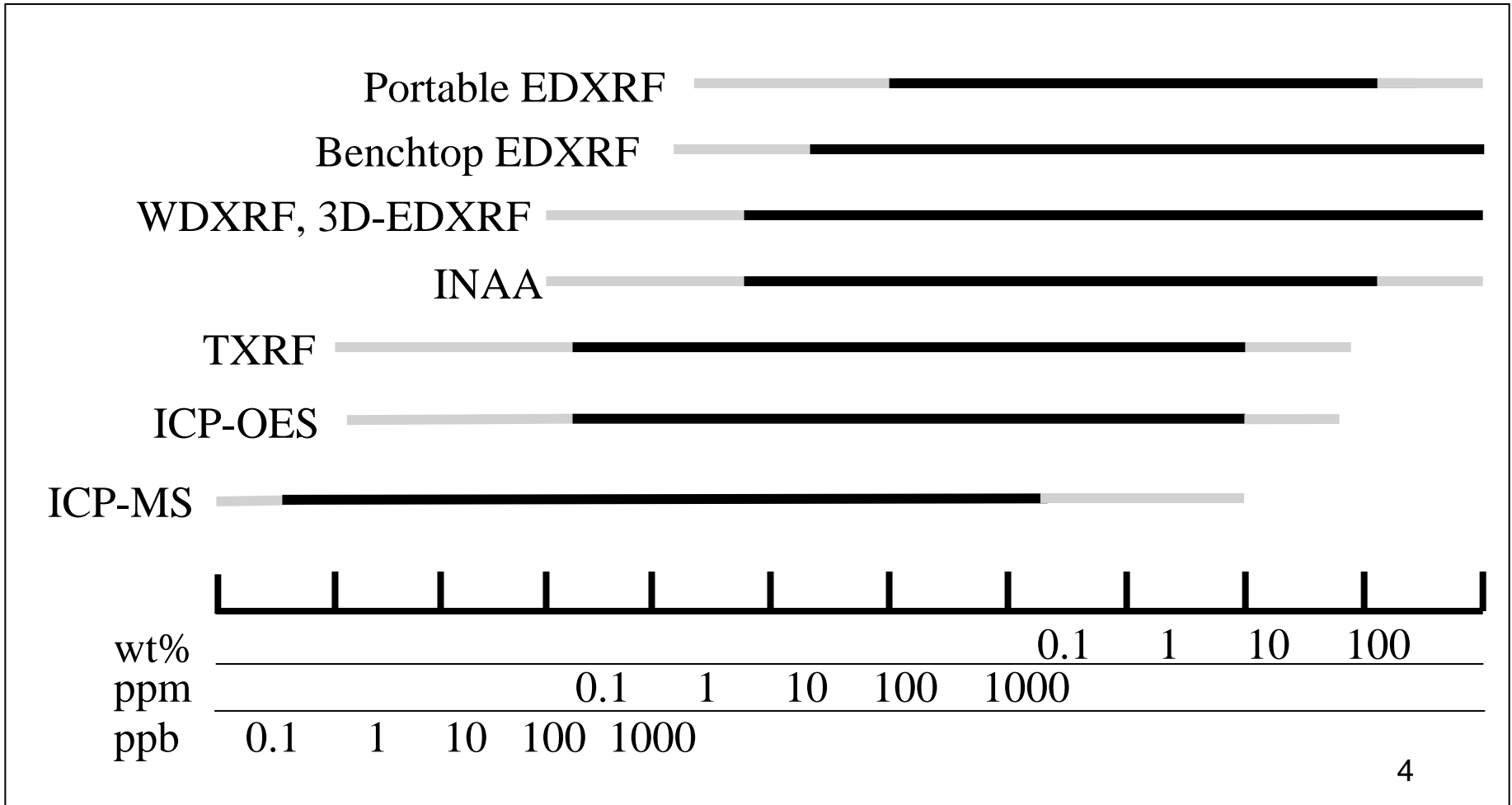- Which method and machine is for you?

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

Portable EDXRF	
Benchtop EDXRF	
WDXRF, 3D-EDXRF	
INAA	
TXRF	
ICP-OES	
ICP-MS	

wt%									0.1	1	10	100
ppm			0.1	1	10	100	1000					
ppb	0.1	1	10	100	1000							

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Some typical spectrometers

	Bruker AXS	Innov'X	PANalytical
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 analysing 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.

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Spectrometer Resolution

- At low energy (medium-long wavelength; >~2Å or <~6 keV), WDXRF is far superior to EDXRF
- At higher energy (shorter wavelength; (<~0.8Å or >~16keV), 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.

Higher energy

Lower energy

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

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.
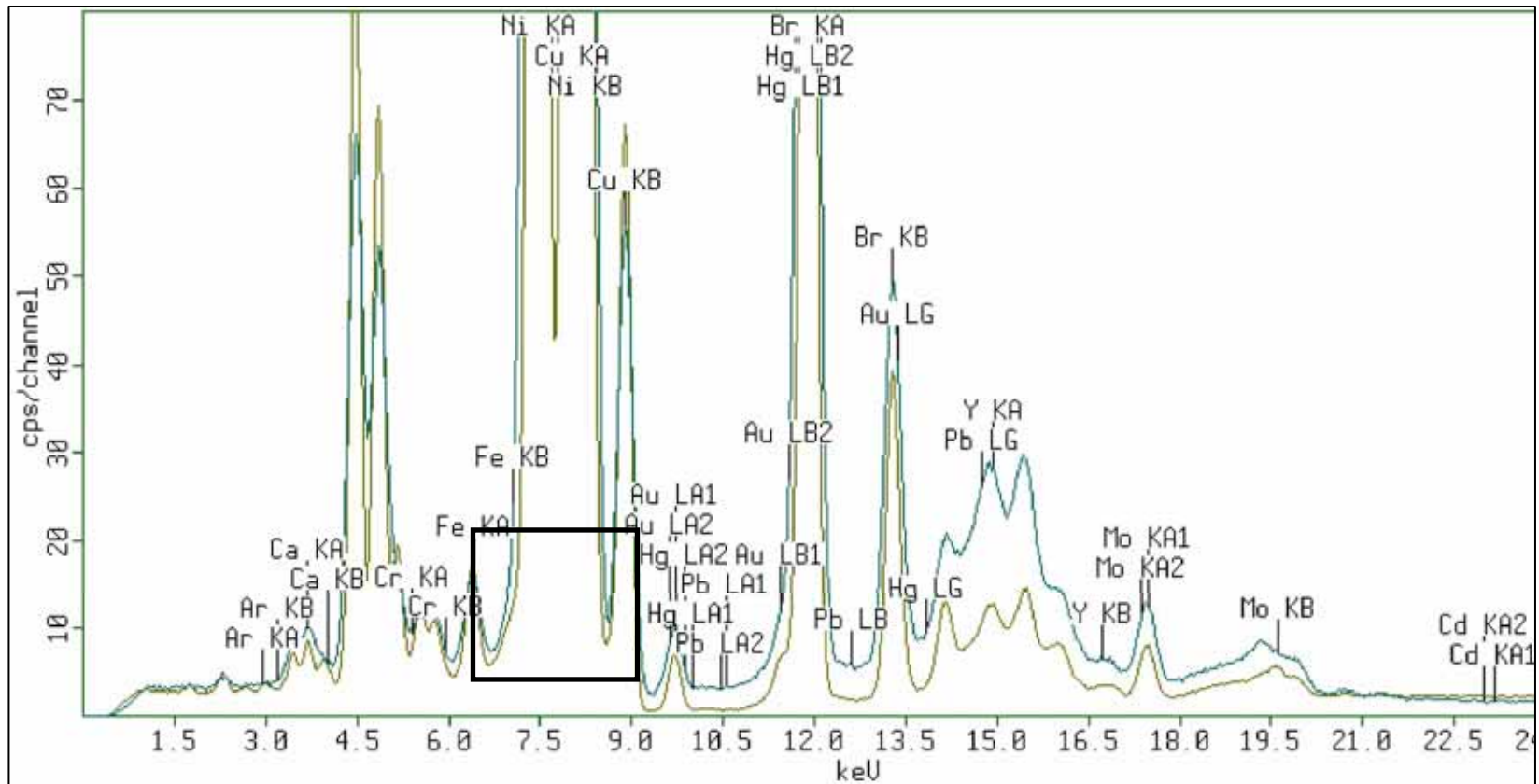
Escape peaks

• 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
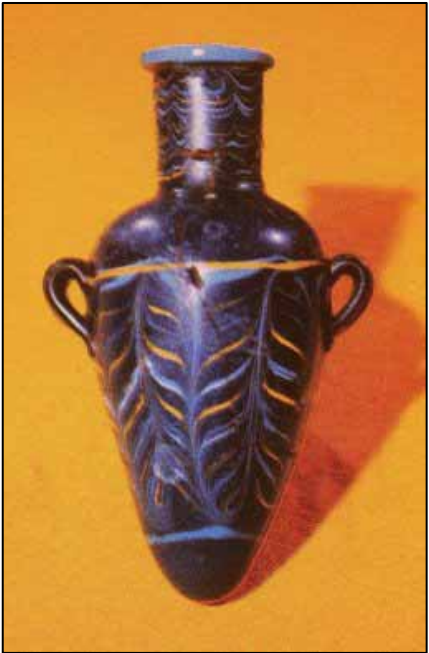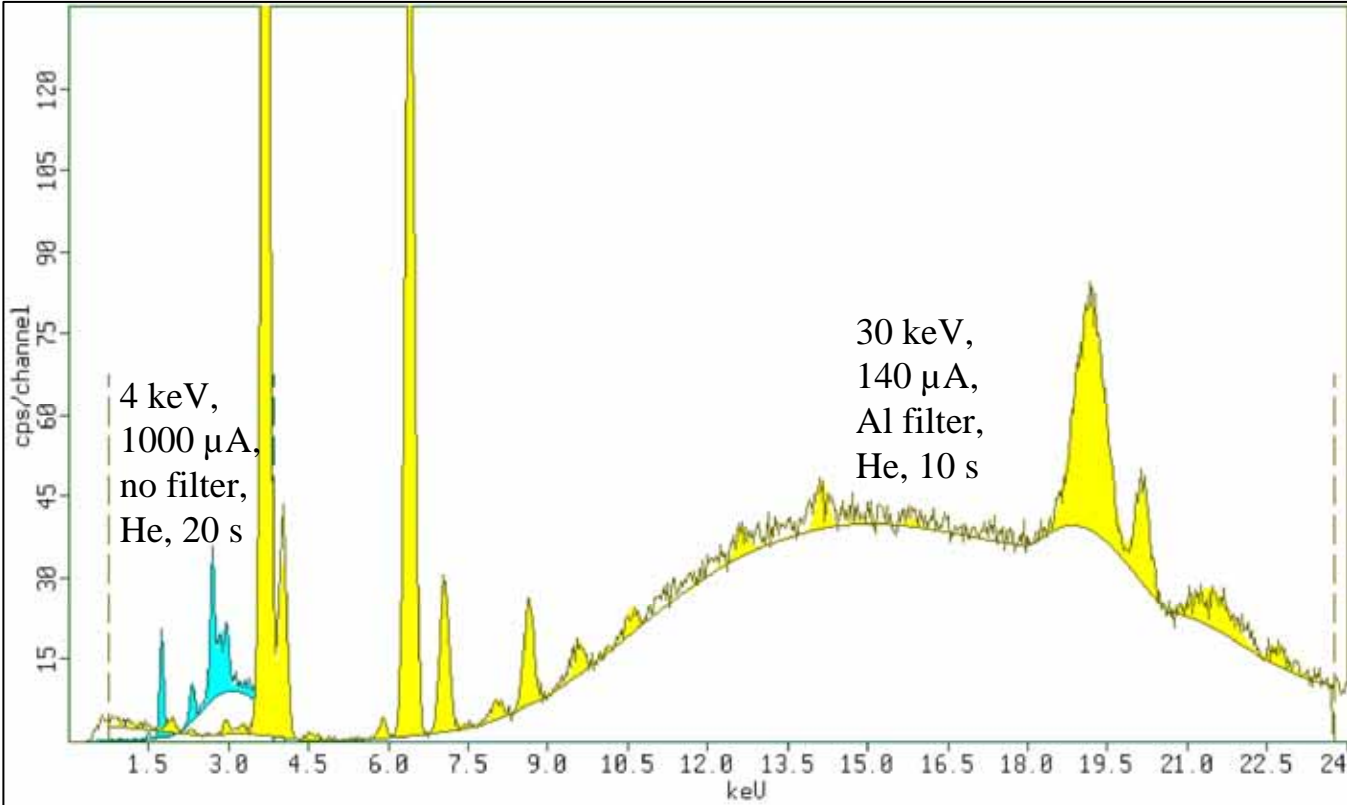
Low energy shelves

• 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.
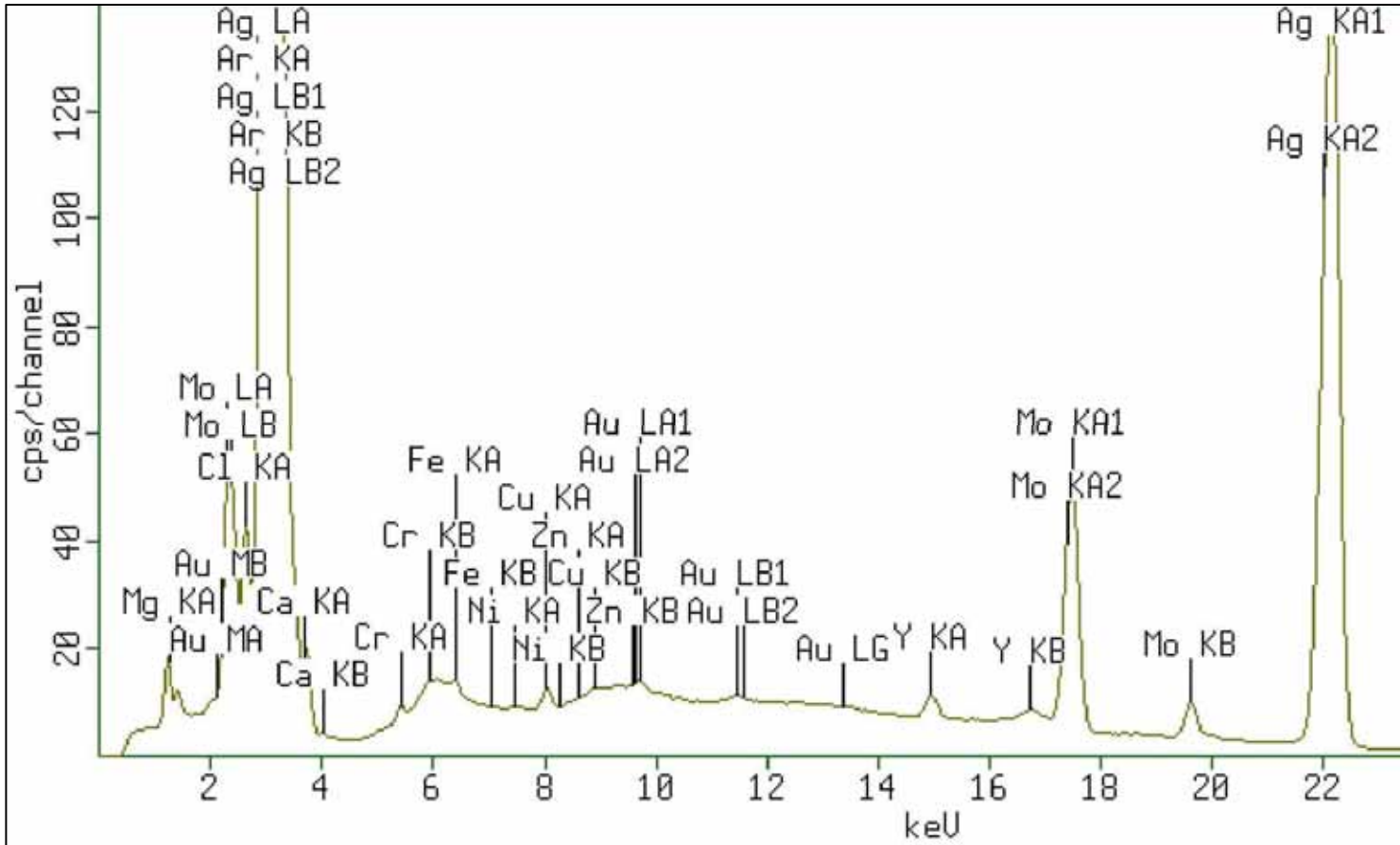
ABS Plastic, MP4, Mo tube, 30 keV, 300 µA, 600 s, air [brown=Cu75µm filter, blue=Al filter]

Examples of spectra

4 keV,
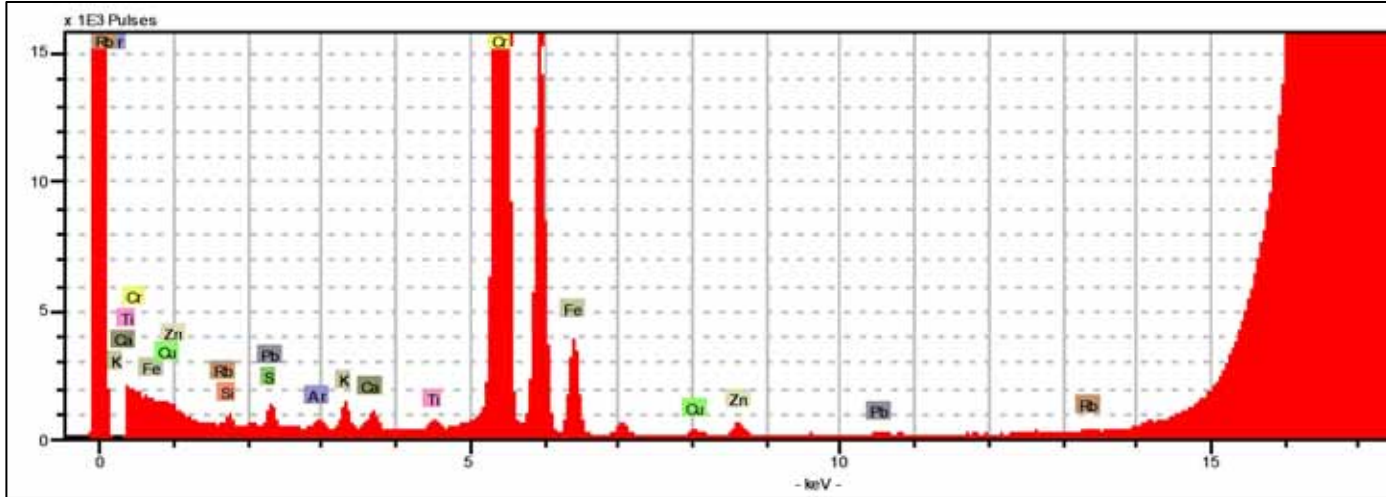1000 µA,
no filter,
He, 20 s

30 keV,
140 µA,
Al filter,
He, 10 s

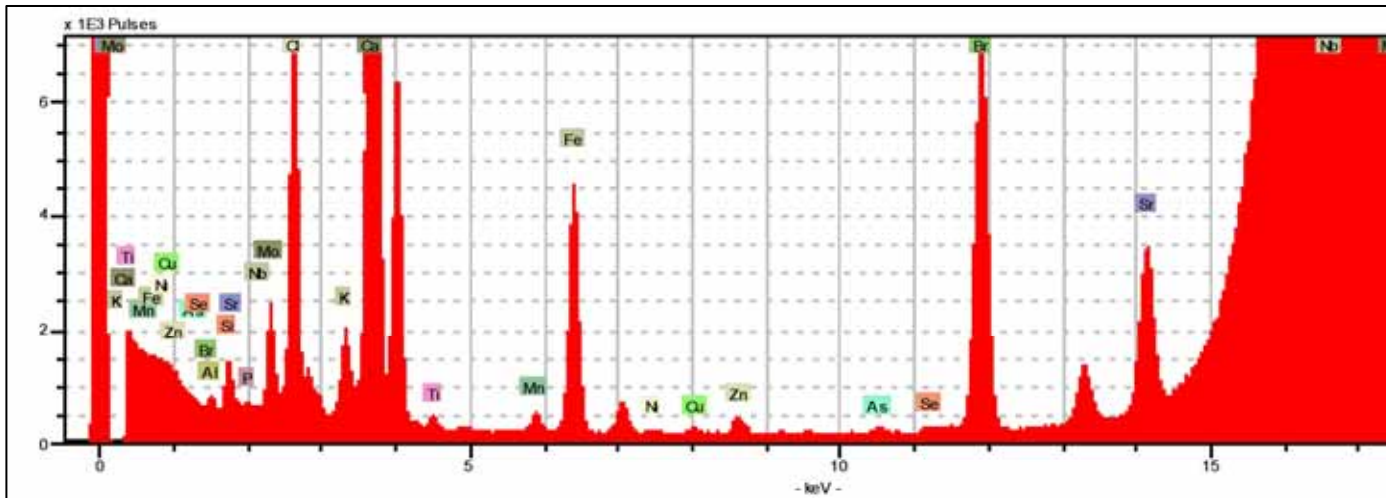Roman Glassware - PANalytical MiniPal4, Rh tube

Examples of spectra

Sterling silver - PANalytical MP4, Mo tube, 30 keV, 20 µA, no filter, air, 1000 s (measured 99.6% Ag)

Examples of spectra

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

Antarctic Ascidian (sea squirt) - Bruker Picofox TXRF, Mo tube, 50 keV, 750 µA, 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

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