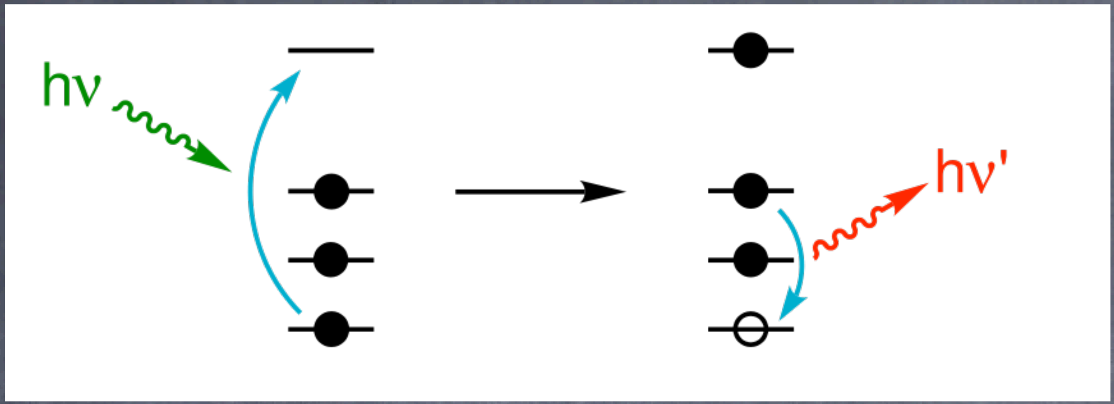
XRF in Handheld Mode

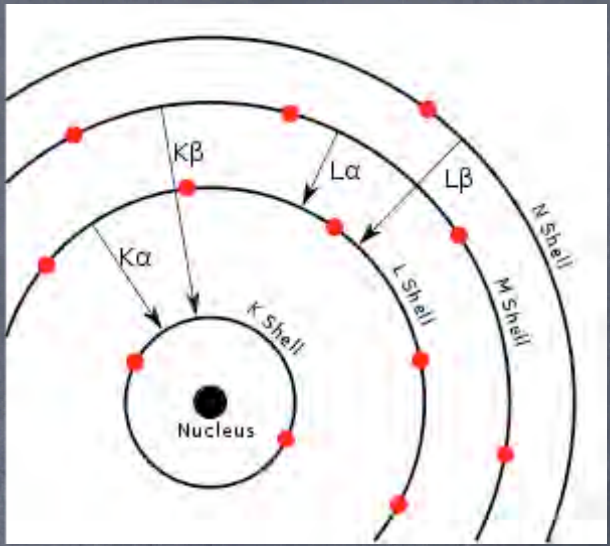
Craig Smith

Outline

- Basic Theory
- Detectors
- Sources
- Detection Limits
- Limitations
- Practicalities

Physics

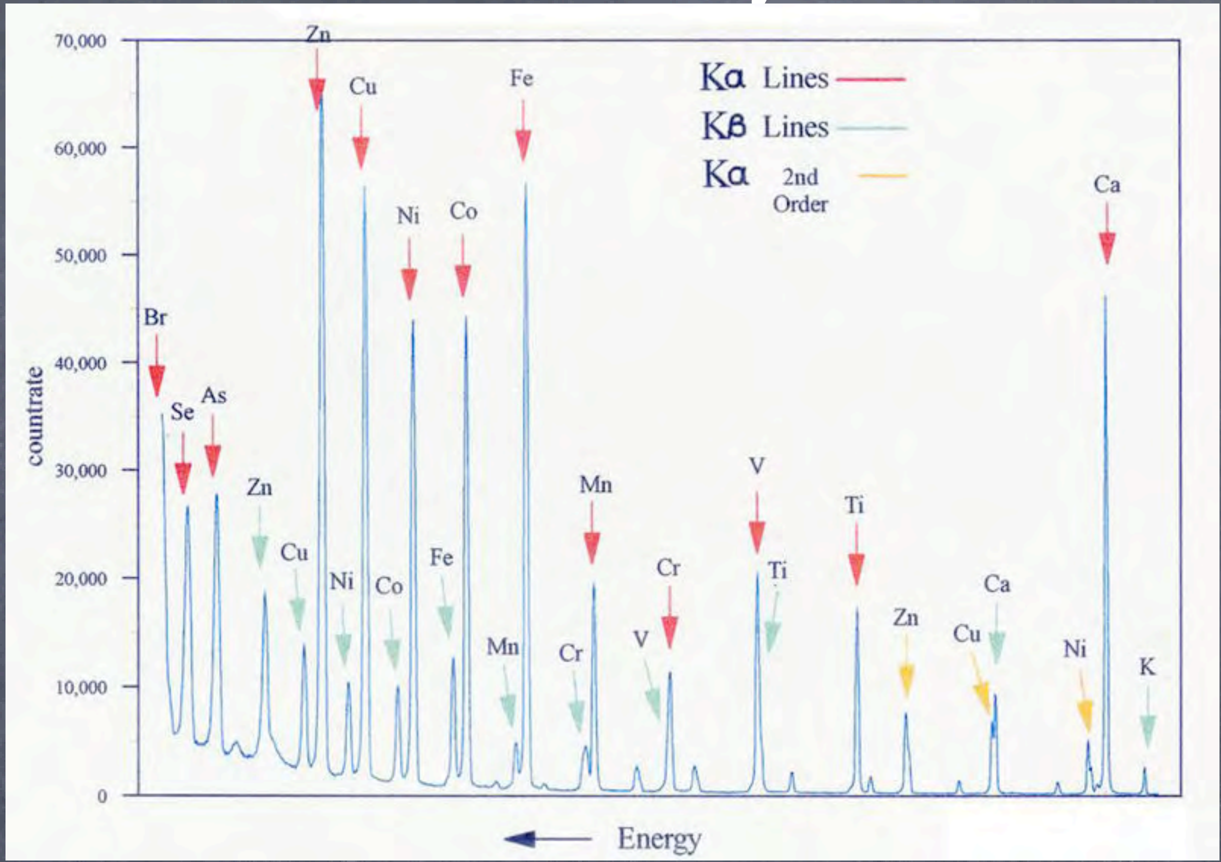




- X-Ray energy is higher than the ionization potential of the inner most electron
- The other electrons then cascade down
- Lines correspond to shells to which they fall
- Kα from L to K shell, Kβ from M to K shell
- Lα from M to L shell, Lβ from N to L shell

http://en.wikipedia.org/wiki/XRF

More Physics



- Energy dispersive XRF Method
  - Multi-channel Analyser Pulse height analysis 2048 channels
  - $\lambda = hc/E\tau$
- Wavelength dispersive XRF Method - Better resolution
  - Scanning Diffraction Grating Monochromator
  - $n\lambda = 2d \sin(\theta)$ [Bragg Equation]

http://en.wikipedia.org/wiki/XRF

Detectors

- Energy Dispersive
  - Photon energy converted directly to pulse height
  - Detected with
    - PIN Diode
    - Si(Li)
    - Ge(Li)
    - Silicon Drift Detector (SDD)
- Wavelength Dispersive
  - Single wavelength passed to photomultiplier (photon counter)
  - Photomultiplier does not depend on wavelength
  - Single photon amplified to a measurable amount

X-Ray Sources

- X-ray Tubes
- Miniature X-ray tubes
  - Niton 50kV tubes
- Cold Cathode Carbon nano-tube X-ray tubes
  - Too low energy (30keV) for high atomic number elements
  - 10e8 photons/s/4π
  - Safer to use
- Pyroelectric Sources
- Radioactive Sources
  - 55Fe, 109Cd and 241Am
  - 3.7e8 photons/s/4π
  - Licensing requirements

X-Ray Sources

Table 1. Radioisotopes commonly used in XRF arrangements.

Isotope	Half-life	Radiation	Energy (keV)	Excited elements
Fe-55	2.7 y	Mn K	5.9	Al-Cr
Co-57	270d	Fe K γ γ γ	6.4 14.4 122 136	<Cf
Cd-109	1.3 y	Ag K γ	22.2 88	Ca-Tc W-U
Am-241	470 y	Np L γ	14-21 26	Sn-Tm

Table 2. Specifications of some X-ray tubes.

Anode material	Voltage (kV)	Current (mA)	Excited elements
Ca (K-rays)	8-10	0.1-1	P, S, Cl
Pd (L-rays)	3-5	0.1-1	P, S, Cl
Pd (K-rays)	35	0.1-1	K-Sn (K-rays), Cd-U (L-rays)
Ti (K-rays)	10	0.1-1	Cl, K, Ca
Mo (K-rays)	30	0.1-1	K-Y (K-rays), Cd-U (L-rays)
W	35	0.1-1	K-Sn (K-rays), Tb-U (L-rays)
W	50	0.1-1	Zn-Ba (K-rays), Tb-U (L-rays)

http://omega.physics.uoi.gr/xrf/english/the_xrf_technique.htm#DL

Detection Limits

- X-ray source flux and energy distribution;
- X-ray source brightness (flux/unit area/unit solid angle);
- X-ray detector geometric efficiency and energy efficiency;
- X-ray detector resolution (peak to background ratio);
- Strong absorption of low energy X-rays in high density matrices;
- Interference of X-ray lines of other elements.
- Somewhere between 10 - 100 ppm

Detection Limits

^{109}Cd source excitation		
Element	**line**	**mg/kg**
Mn	K	354
Fe	K	424
Co	K	354
Ni	K	116
Cu	K	80
Zn	K	63
Ga	K	58
Rb	K	13
Sr	K	14
Y	K	9
Zr	K	9
Nb	K	6
Pb	L	39

^{55}Fe source excitation		
Element	**line**	**mg/kg**
K	K	360
Ca	K	225
Ti	K	120
V	K	49
Cr	K	1080
^{241}Am source excitation		
Ba	K	21
La	K	ca. 16
Ce	K	14

Lines used

element	line	wavelength - nm	element	line	wavelength - nm	element	line	wavelength - nm
Li	$K\alpha$	22.8	Ni	$K\alpha_1$	0.1658	I	$L\alpha_1$	0.3149
Be	$K\alpha$	11.4	Cu	$K\alpha_1$	0.1541	Xe	$L\alpha_1$	0.3016
B	$K\alpha$	6.76	Zn	$K\alpha_1$	0.1435	Cs	$L\alpha_1$	0.2892
C	$K\alpha$	4.47	Ga	$K\alpha_1$	0.1340	Ba	$L\alpha_1$	0.2776
N	$K\alpha$	3.16	Ge	$K\alpha_1$	0.1254	La	$L\alpha_1$	0.2666
O	$K\alpha$	2.362	As	$K\alpha_1$	0.1176	Ce	$L\alpha_1$	0.2562
F	$K\alpha 1$	1.832	Se	$K\alpha_1$	0.1105	Pr	$L\alpha_1$	0.2463
Ne	$K\alpha 1$	1.461	Br	$K\alpha_1$	0.1040	Nd	$L\alpha_1$	0.2370
Na (11)	$K\alpha 1,2$	1.191	Kr	$K\alpha_1$	0.09801	Pm	$L\alpha_1$	0.2282
Mg	$K\alpha 1,2$	0.989	Rb	$K\alpha_1$	0.09256	Sm	$L\alpha_1$	0.2200
Al	$K\alpha 1,2$	0.834	Sr	$K\alpha_1$	0.08753	Eu	$L\alpha_1$	0.2121
Si	$K\alpha 1,2$	0.7126	Y	$K\alpha_1$	0.08288	Gd	$L\alpha_1$	0.2047
P	$K\alpha 1,2$	0.6158	Zr	$K\alpha_1$	0.07859	Tb	$L\alpha_1$	0.1977
S	$K\alpha 1,2$	0.5373	Nb	$K\alpha_1$	0.07462	Dy	$L\alpha_1$	0.1909
Cl	$K\alpha 1,2$	0.4729	Mo	$K\alpha_1$	0.07094	Ho	$L\alpha_1$	0.1845
Ar	$K\alpha 1,2$	0.4193	Tc	$K\alpha_1$	0.06751	Er	$L\alpha_1$	0.1784
K	$K\alpha 1,2$	0.3742	Ru	$K\alpha_1$	0.06433	Tm	$L\alpha_1$	0.1727
Ca	$K\alpha 1,2$	0.3359	Rh	$K\alpha_1$	0.06136	Yb	$L\alpha_1$	0.1672
Sc	$K\alpha 1,2$	0.3032	Pd	$K\alpha_1$	0.05859	Lu	$L\alpha_1$	0.1620
Ti	$K\alpha 1,2$	0.2749	Ag	$K\alpha_1$	0.05599	Hf	$L\alpha_1$	0.1570
V	$K\alpha_1$	0.2504	Cd	$K\alpha_1$	0.05357	Ta	$L\alpha_1$	0.1522
Cr	$K\alpha_1$	0.2290	In	$L\alpha_1$	0.3772	W	$L\alpha_1$	0.1476
Mn	$K\alpha_1$	0.2102	Sn	$L\alpha_1$	0.3600	Re	$L\alpha_1$	0.1433
Fe	$K\alpha_1$	0.1936	Sb	$L\alpha_1$	0.3439	Os	$L\alpha_1$	0.1391
Co	$K\alpha_1$	0.1789	Te	$L\alpha_1$	0.3289	Ir	$L\alpha_1$	0.1351

http://en.wikipedia.org/wiki/XRF

Process Issues

- Analysis is able to analyze all chemical elements with atomic number Z larger than 12
- Limited by low energy of fluorescence radiation attenuated by air
- Requirements for vacuum or lowered air pressure
- Depends on source energy to ionise atom
- Low count rate compared to incident radiation
- Measurement Time
- It is not sensitive to the chemical binding, i.e. it not distinguishing the chemical compound

Sample Measurement Issues

- Interference Effects
- Sample Heterogeneity
- Measurement Time
- Strength of Source
- Quality of Detector

Limitations

- Penetration depth
  - Sub-millimetre or less depending on material
  - Cleanliness of surface and homogeneity
- Range of elements that can be measured
- X-Ray sources and power
  - Isotopic sources
  - Lifetime
  - OHSE Restrictions
- Accessibility to Material (such as borehole)

Weathering Effects

Fresh

Weathered

Surface

Philip J. Potts
The Open University, Milton Keynes, MK7 6AA

Sampling Methods

- Conventional analysis
  - Samples collected and returned to laboratory (by the investigator).
  - Sample crushed, homogenised (often by a technician).
  - Sample analysed using automated programme supervised by laboratory staff.
  - Results are returned to the investigator after a turnround time of typically a few days (sometimes years).
  - Results are representative of the mass of the hand specimen submitted for analysis.
  - Investigator often does not understand the analytical laboratory methods, laboratory staff do not always understand the provenance of the sample.
- PXRF
  - Sampling and analysis are one process (undertaken by or under the direction of the investigator).
  - No (or little) sample preparation is possible - only sample selection.
  - Results are immediately available to the investigator.
  - Analytical result is representative of the small mass of material immediately in contact with the PXRF.
  - Investigator must understand both sampling protocol and limitations of the PXRF method.

Number of Samples

Rock type	Dolerite	Quartz andesite	Micro-grani	Medium grained granite	Coarse grained granite
Maximum mineral size (mm)	1 (to 2)	1 to 3	1 to 3	3 to 4	7 to 35
n for 5% precision	2	3	3	4	82
n for 2% precision	8	20	17	23	512

Philip J. Potts
The Open University, Milton Keynes, MK7 6AA