Relieving Ambiguity by using Particle-Induced X-ray Emission self-consistently with Particle Scattering

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Excitation: ions (PIXE), electrons (SEM-EDS, AES), photons (XRF, XPS)

De-excitation: photons (XRF, PIXE, SEM-EDS), photoelectrons (XPS), Auger electrons (AES), mixed possibilities through the Coster-Kronig process

Taken from the Wikipedia article on Auger Electron Spectroscopy 18Feb09
Auger_Process.svg from Wikipedia Commons.
PIXE process II
exciting the atom with protons

Position in 1988 (!)

ECPSSR theory has been used to get ionisation cross-sections for both H and He
Semi-classical approximation treats Coulomb repulsion “rather exactly” (H.Paul) and improves on ECPSSR for high Z (or low proton energy)
He can be treated as ~ H with $\frac{1}{4}$ of the energy with $4\times$ionisation probability ($Z^2$)

Figure 2.1 The K- and L-shell ionization cross-sections as functions of proton energy $E$ and target atom. The values are the theoretical ECPSSR predictions [6]

ECPSSR predictions from D.D.Cohen & M.Harrigan At. Data & Nucl. Data Tables 33, 1985, 255
Atomic de-excitation starts by electron falling radiatively (or non-radiatively) into the vacancy.

Photons produced in the radiative process are characteristic of the element.

Photon energies for the three main line groups are well known.

Figure 1.2 Atomic level diagram showing the main K and L X-ray transitions. [4] Reproduced by permission of the author.


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The K- and L-shell fluorescence yields as functions of atomic number Z

PIXE as an IBA technique
what are the spectra like?

- 1.9 MeV protons, Si(Li) detector at 135° with 130μm Be filter
- BCR126a lead glass standard:
- Si, K, Ca, Ba, Zn, Pb = 27, 8.3, 0.74, 0.82, 0.93, 22.3 (wt%)
- Note ordinate in log scale

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PIXE as an IBA technique
how to use it?
how to interpret the spectra?

• High cross-section gives high absolute sensitivity (~fg with $\mu$-beam)
  – trace element sensitivity means EDX not WDX is appropriate
  – rapid mapping with $\mu$-beam
• Background: secondary electron Bremsstrahlung
  – low signal:noise gives very low detection limits ($\mu$g/g)
  – ‘no’ Brehmsstrahlung from the primary beam
• Absorption
  – highly wavelength and matrix dependent
• Raw information is characteristic line intensities
  – no direct depth information
• Indirect depth information
  – from “differential PIXE”: varying energy changes excitation volume
  – from “differential PIXE”: varying geometry changes absorption
PIXE as complementary in IBA

In layered structures, need depth profile to correctly calculate PIXE absorption

**PIXE strength**
- High sensitivity
- Excellent specificity

**BS strength**
- Traceable accuracy
- Excellent depth resolution

**BS weakness**
- Low sensitivity
- Poor mass resolution

**PIXE weakness**
- Poor traceability
- Poor depth resolution

NB: PIXE information depth is usually significantly larger than for BS

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Self-consistent PIXE/RBS/EBS

- **DataFurnace**: fitting code based on the simulated annealing algorithm or a local minimisation algorithm; molecules, roughness, *multiple spectra*, non-Rutherford backscattering

- Use **DataFurnace** (Jeynes++, *JPhysD* 2003; 36: R97-R126)

- Use **LibCPIXE** (Pascual-Izarra++, *NIMB* 2006; 249: 820-822)


- Add **PIXE module to NDF** (Pascual-Izarra++, *NIMB* 2006; 249: 780-783)

- Get X-ray line areas from **GUPIX** using **OMDAQ** (Campbell++, see Blaauw++ *NIMB* 2002; 189: 113-122; Grime, *NIMB* 1995; 109: 170-174)

- Check NDF against **GUPIX**, and critically compare **PIXE** with **SEM-EDX** (Bailey, Jeynes, Grime++, ‘accepted’ in *X-ray Spectrometry*)

**PIXE / BS is VERY NEW!**
Towards truly simultaneous PIXE and RBS analysis of layered objects in cultural heritage

C. Pascual-Izarra (Madrid), N. P. Barradas, M. A. Reis (Lisbon), C. Jeynes (Surrey), M. Menu, B. Lavdrine, J. J. Ezrati, S. Röhrs (Louvre)


Corrosion products demonstrated by PIXE/RBS/EBS to be tin oxide in a tin/lead matrix
Characterization of paint layers by simultaneous self-consistent fitting of RBS/PIXE spectra using simulated annealing

L. Beck (Louvre), C. Jeynes (Surrey), N.P. Barradas (Lisbon)
Roughness


- Beam re-entering through surface asperities gives extra surface energy loss due to extra pathlength $x$
- Generate a general rough surface giving a pathlength density function $f(x)$
- Characterise roughness with TWO PARAMETERS: “sharpness” $\sigma$ and “scale” $p$
- Parameterise $f(x)$ explicitly using extensive Monte Carlo calculations

\[
    f(x) = (1 - n)\delta(x) + n \frac{b^{a+1}}{\Gamma(a + 1)} x^a \exp(-bx)
\]

SIMNRA (and NDF) can simulate only some of the roughness effect
New algorithm calculates the high energy effect and the lower max yield

New algorithm correctly calculates the smearing of the EBS resonances “R”. The effect on the depth profiles is LARGE

- Most real samples are ROUGH!
- This algorithm can extract scale and sharpness of real rough samples from BS spectra without MonteCarlo
- Valid for RBS, EBS, ERD, PIXE, NRA
- Correct depth profiles!

www.surreyibc.ac.uk
RBS/EBS/PIXE measurement of single-walled carbon nanotube modification by nitric acid purification treatment

J.C.G. Jeynes, C. Jeynes, K.J. Kirkby, M. Rümmeli, S.R.P. Silva


O and N quantified by PIXE/RBS/EBS in the presence of mixed heavy metal catalyst content of CNT with heavy roughness

Catalyst contains Pt, Rh, Re, Fe, Cu, Cl, Na. Roughness effects marked “R”

SEM

RBS

SWCNT on mylar

Fitted depth profile
Characterisation of thin film chalcogenide PV materials using MeV ion beam analysis

Chris Jeynes, G. Zoppi, I. Forbes, M. J. Bailey, N. Peng

SuperGen conference, Shanghai, April 2009

- CIAS semiconductor on Mo electrode
- Precursor material (not selenided yet)
- Al invisible in backscattering
- Strong layering: PIXE uninterpretable without profile independently available
- Differential PIXE to profile Al
- Essential to fit roughness to reproduce RBS spectra
- Good fit essential for reliable profile

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Impact glass from 800,000 year old meteor strike crater at Mt.Darwin, Tasmania
Inclusions are Carbon and Silicon (silica) rich: confirmed by PIXE/EBS
Inclusions highly heterogeneous:
silica observed by EBS/PIXE

Silica (quartz by XRD) not observable without PIXE. Unequivocal profiling down to ~15μm with EBS
NRP (PIGE) of metal boro-silicide sample

- Sample structure from RBS (boron content poorly determined)
- Co/Fe=3.8 from 2.2MeV PIXE
- Direct PIGE signal for B with a proton beam scanned 0.1-0.3 MeV

Result is:
M:B:Si = 26:58:16

DataFurnace integrates RBS/PIXE/PIGE for self-consistent analysis

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Discussion

- BS probes relatively shallow: PIXE probes deeper (no energy loss on exit path, PIGE probes deeper still (no absorption on exit)
- PIXE + BS gives sensitivity to all elements (except F, Na)
- PIXE + BS is now interpretable even for complex samples
- Roughness can be partially modelled, correct algorithm available. When correct algorithm is implemented any sample will be solvable
- PIXE is useful to relieve ambiguity in broad beam RBS/EBS
- RBS/EBS is useful to relieve ambiguity in $\mu$beam PIXE
- Evaluated cross-sections available on SigmaCalc for EBS/PIXE
- NB: low backscattering count rates in $\mu$beam does not preclude good analysis