The use of x-ray photoelectron spectroscopy for coal characterisation

Dane Sexton
PhD Student
Cardiff University School of Engineering

Supervisors: Dr. Richard Marsh, Dr. Julian Steer

Coal analysis and operability in iron and steel

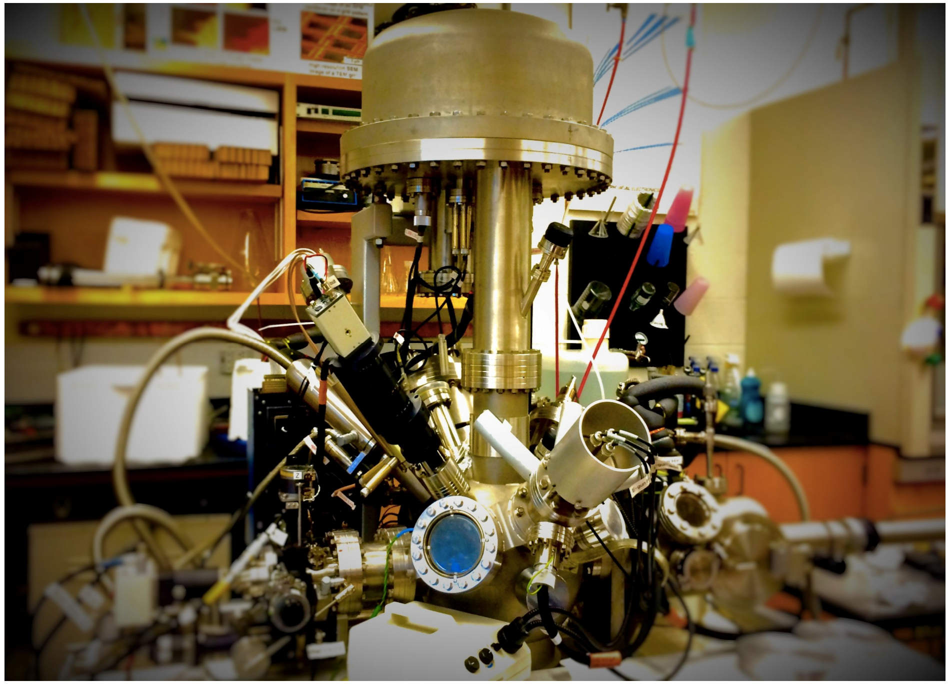
Overview

- Introduction to XPS
- Equipment
- Applications

- Aim of the talk is to introduce XPS as a method for coal characterisation
- Provide examples of various uses of XPS and how they have been applied in coal research

What is X-ray photoelectron spectroscopy?

- Surface analysis technique
- Depth 5-10nm
- Non-destructive
- Used to determine electronic structure of atoms and molecules
- High-energy x-rays can eject core electrons
- Typically used to analyse inorganic compounds, metals, and polymers
- Utilises photoelectric process

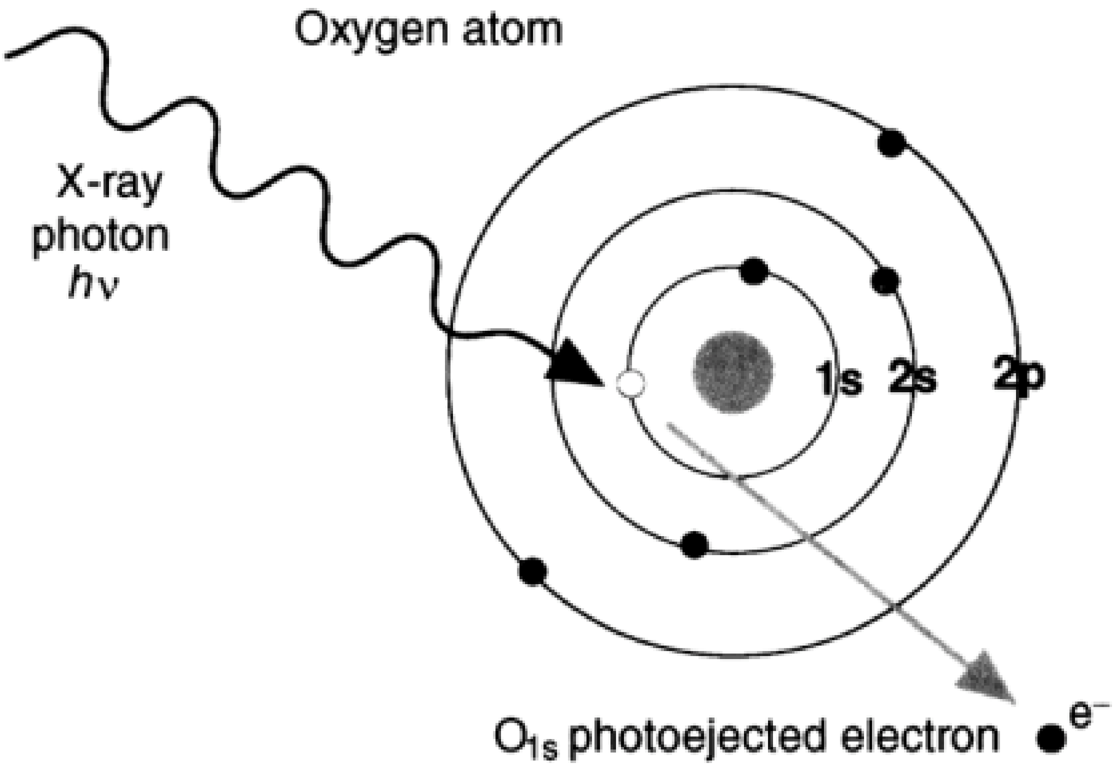


Sites.udel.edu

Photoelectric process

- The effect was honed by Kai Siegbahn in the 60s who was awarded a Nobel Prize for his work developing XPS

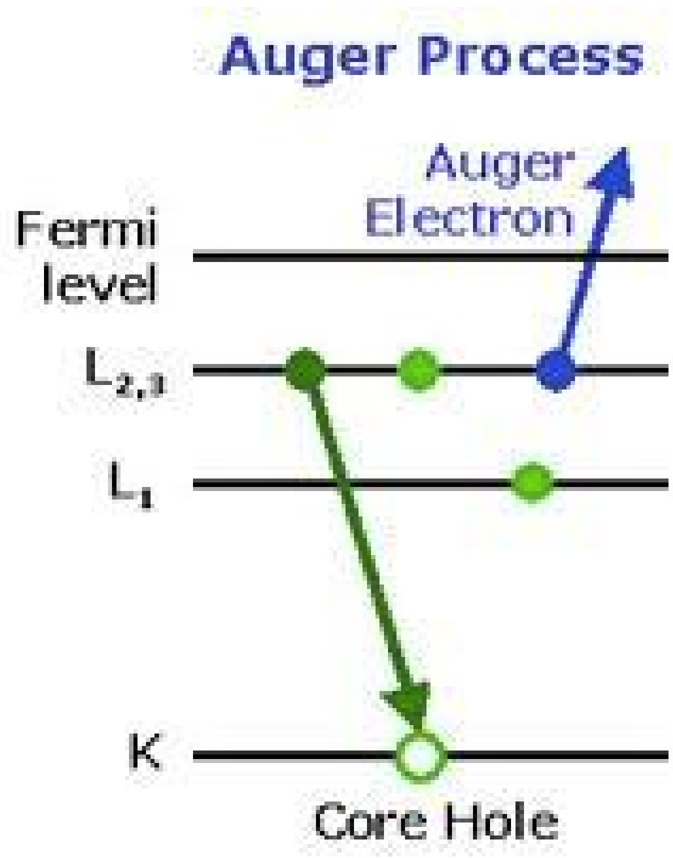
- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.)



www.plasma.de

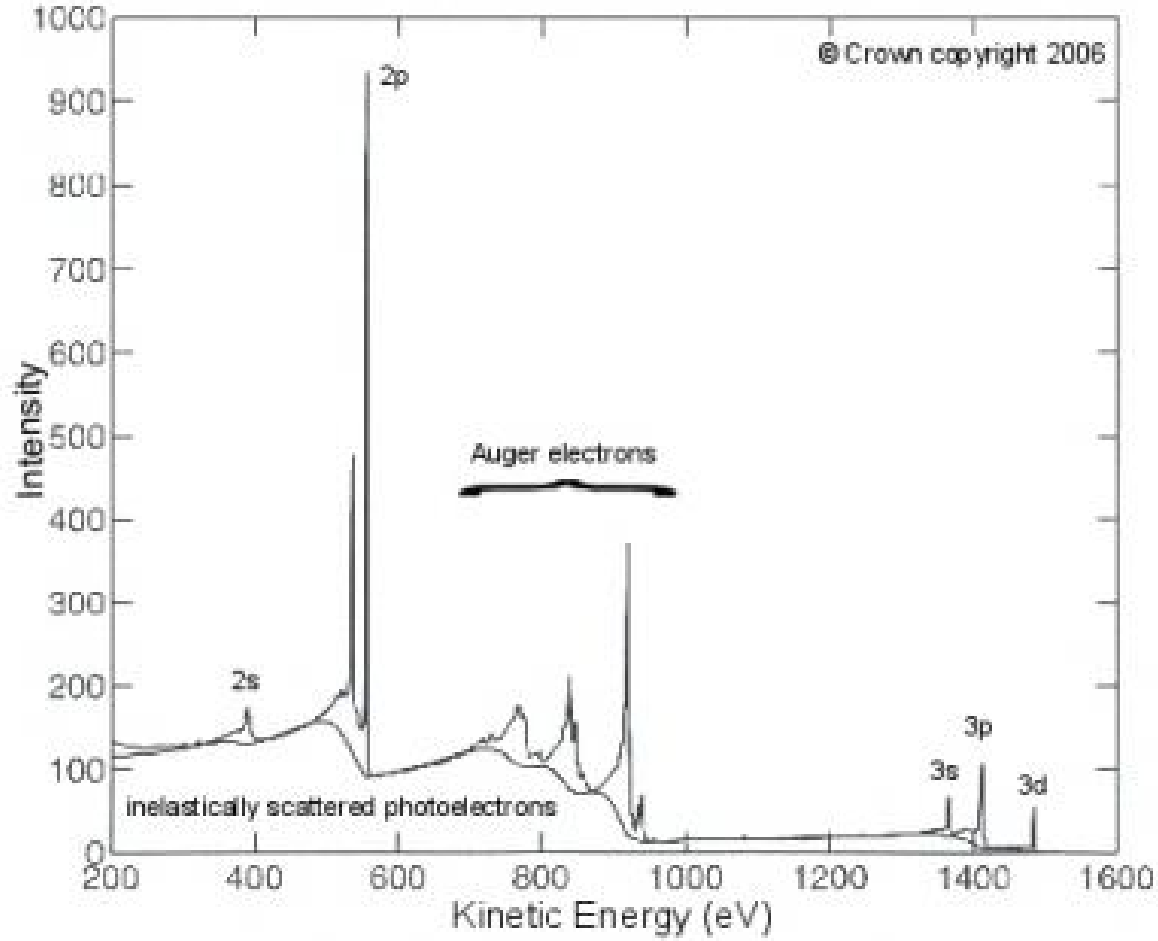
X-ray induced Auger electron

- Following the photoelectron emission, the atom will release energy through ejection of an Auger electron
- A valence electron will fill the space of the photoelectron whilst another electron will be emitted to compensate for this – an Auger electron
- Secondary electron effect



Lpdlabservices.co.uk

XPS energy scale



Copper XPS wide survey spectrum *(National Physical Library)*

- The XPS instrument measures the kinetic energy of all collected electrons, both *photoelectrons*, and *Auger* electrons
- An XPS spectrum will show both XPS (photoelectron) peaks and Auger peaks

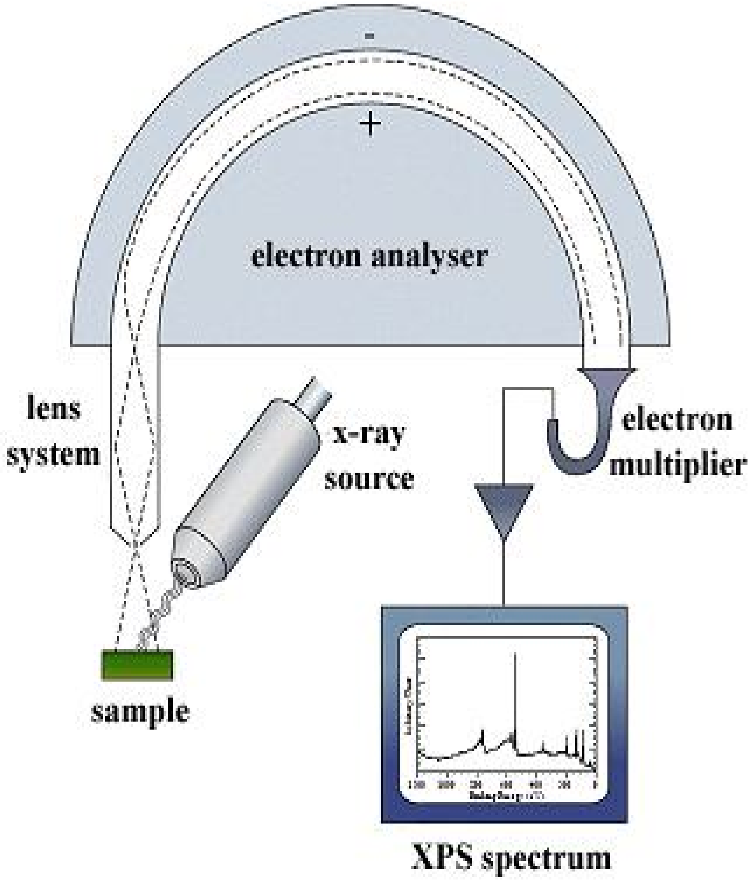
XPS energy scale – binding energy

- Each binding energy (eV) is known to correlate to a specific element/chemical status

$$BE = h\nu - KE - \phi_{spec}$$

- *Binding energy (eV) is the energy required to remove an electron from an atom, a molecule, or an ion*
- This allows us to determine what elements are present and in what quantities

Equipment



Astamuse.com

- Ultra-high Vacuum chamber (UHV) required to increase mean free path for electrons
- This is to ensure the photoelectron's kinetic energy will not be significantly altered

Applications

- Elemental identification
- Chemical state/bonding changes
- Depth profiling
- XPS imaging

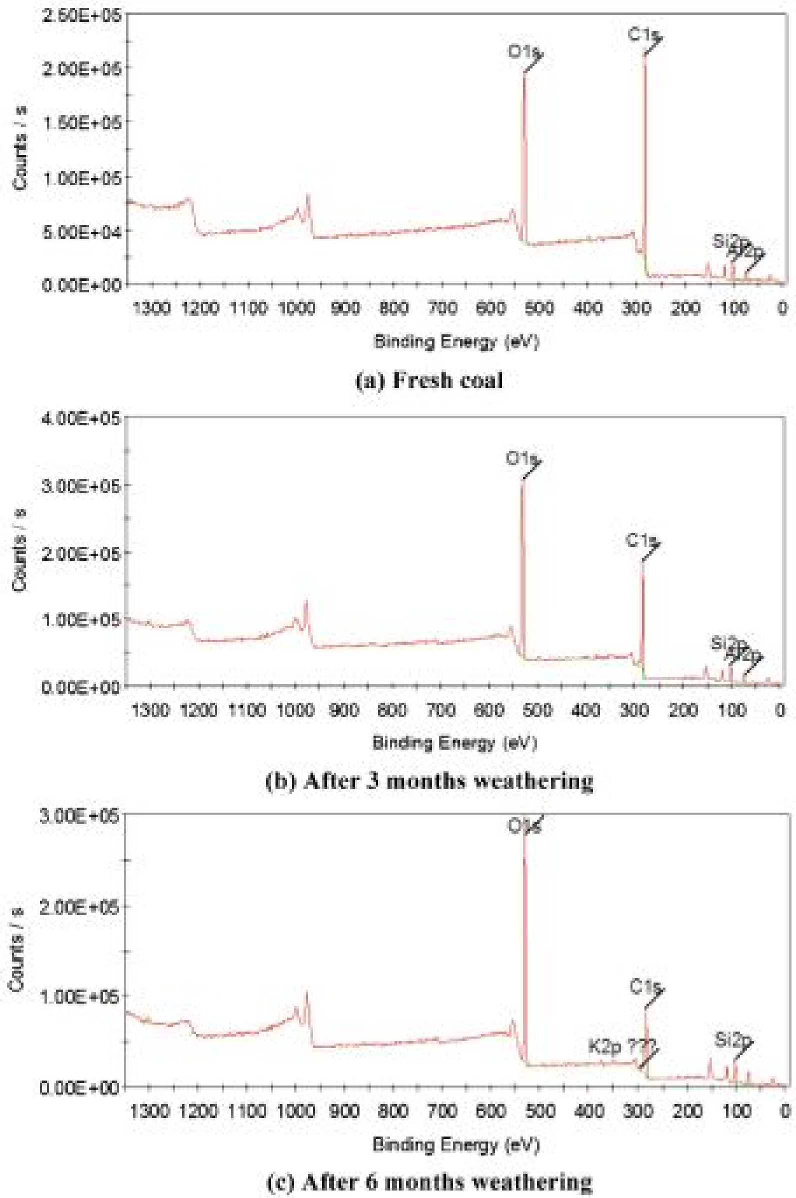
Elemental identification

- What elements exist on the surface
- Quantities of elements
- Effective method of detecting surface contamination

Element	$2p_{3/2}$ (eV)	3p (eV)
Fe	707	53
Co	778	60
Ni	853	67
Cu	933	75
Zn	1022	89

- XPS cannot identify hydrogen peaks – no core electron
- *Electron – nucleus attraction (binding energy) used to identify the elements*

Surface effects of natural weathering after 3/6 months



- Wide survey spectrum to view multiple element peaks at once
- C1s peak intensity decreases – indication of decrease in amount of organic materials on surface
- O1s peak intensity increases
- Surface contents of Al and Si increased with weathering

Xia et al (2014)Investigation of changes in surface properties of bituminous coal during natural weathering processes by XPS and SEM

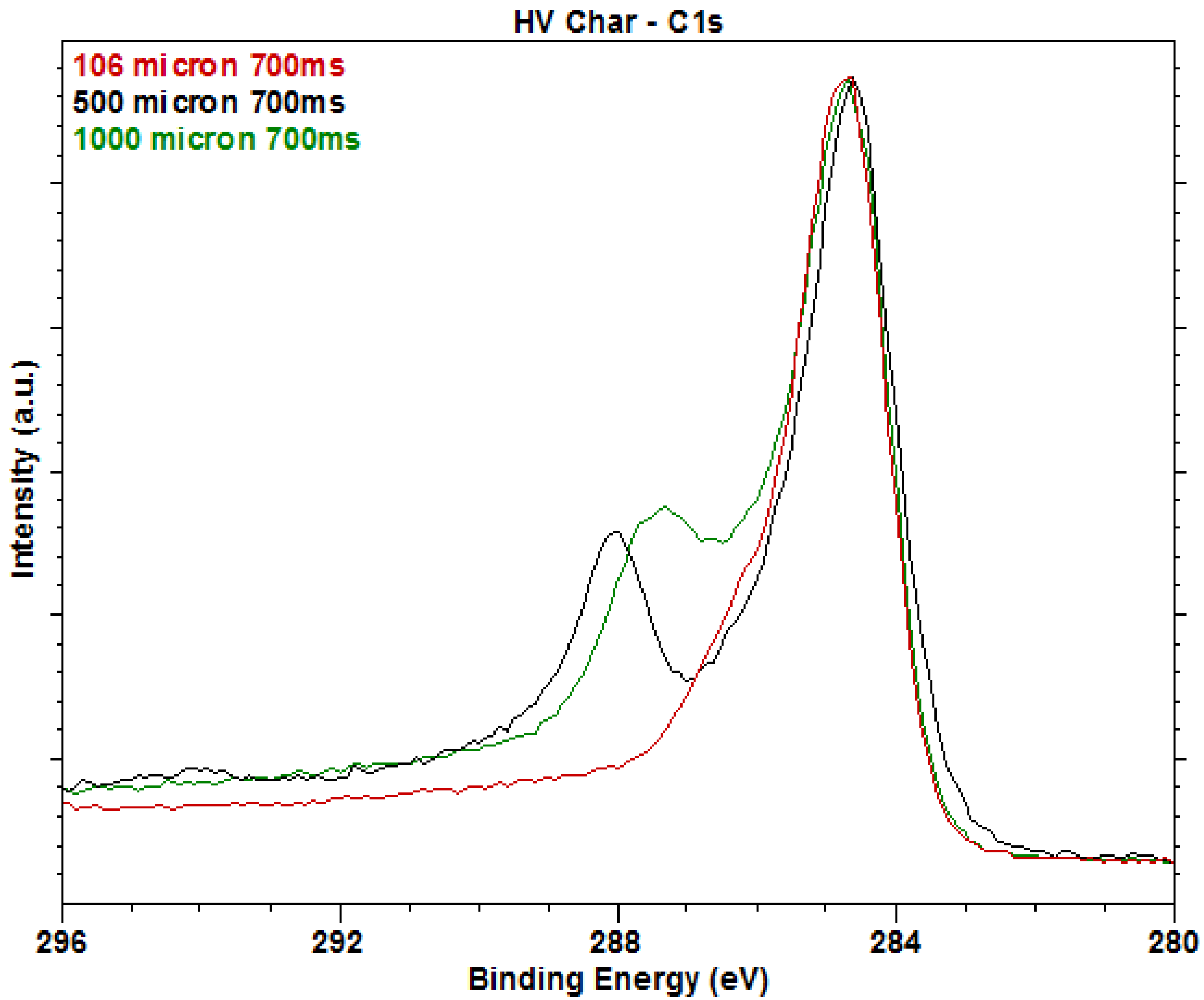
Chemical bonding status

- Each element and type of bond has its own binding energy
- By evaluating the intensity of each binding energy peak we can determine the quantities of certain materials

Functional group	C1s Binding energy (eV)
hydrocarbon C-H, C-C	285.0
amine C-N	286.0
alcohol, ether, C-O-H, C-O-C	286.5
Cl bound to C C-Cl	286.5
F bound to C C-F	287.8
carbonyl C=O	288.0

Surface bonding variation with particle size – *C1s* peak spectra

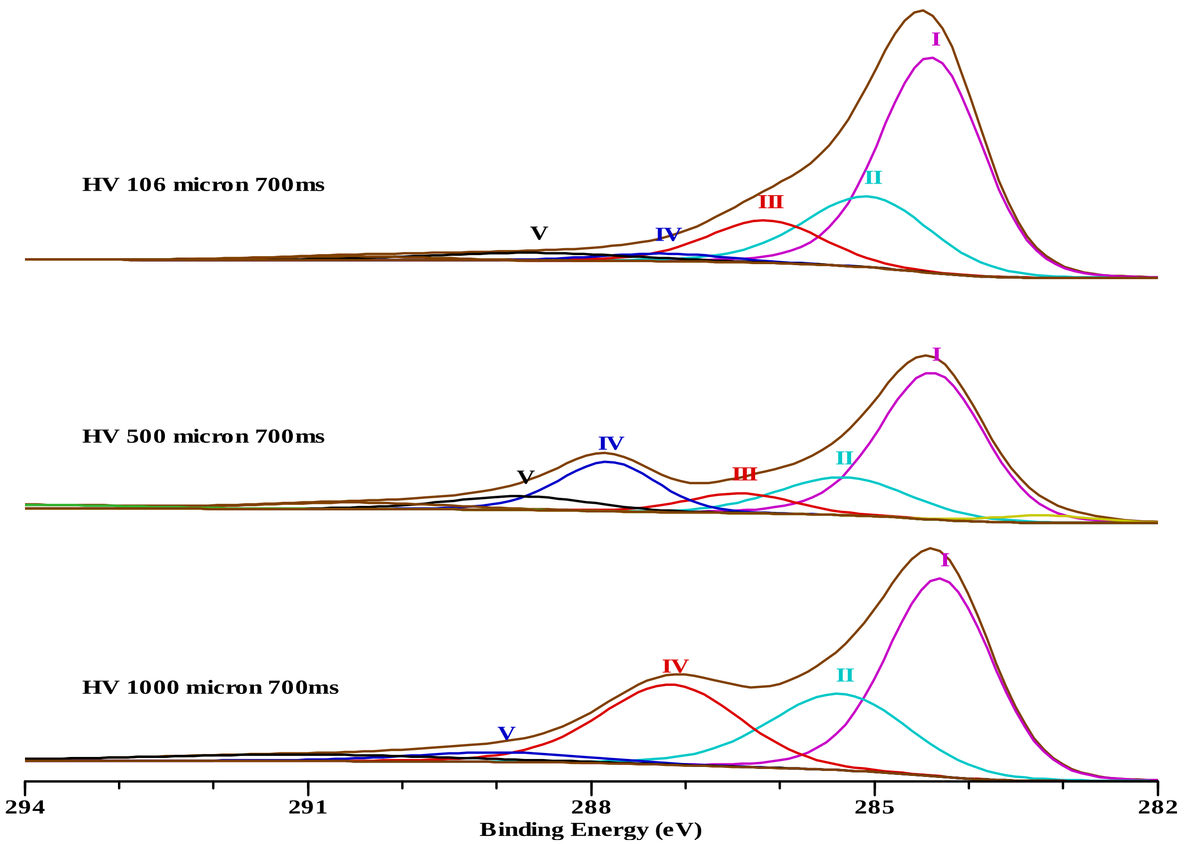
- 3 different Particle size coal chars created in a drop tube furnace to simulate blast furnace coal injection
- <1mm, <500µm, <106µm
- Two larger size chars have bimodal distributions
- Grinding coals to smaller particle size reduced oxygen-carbon bonding on surface
- Surface oxygen species have been found to impact & enhance coal reactivity



Steer et al,(2015)The effects of particle grinding on the burnout and surface chemistry of coals in a drop tube furnace

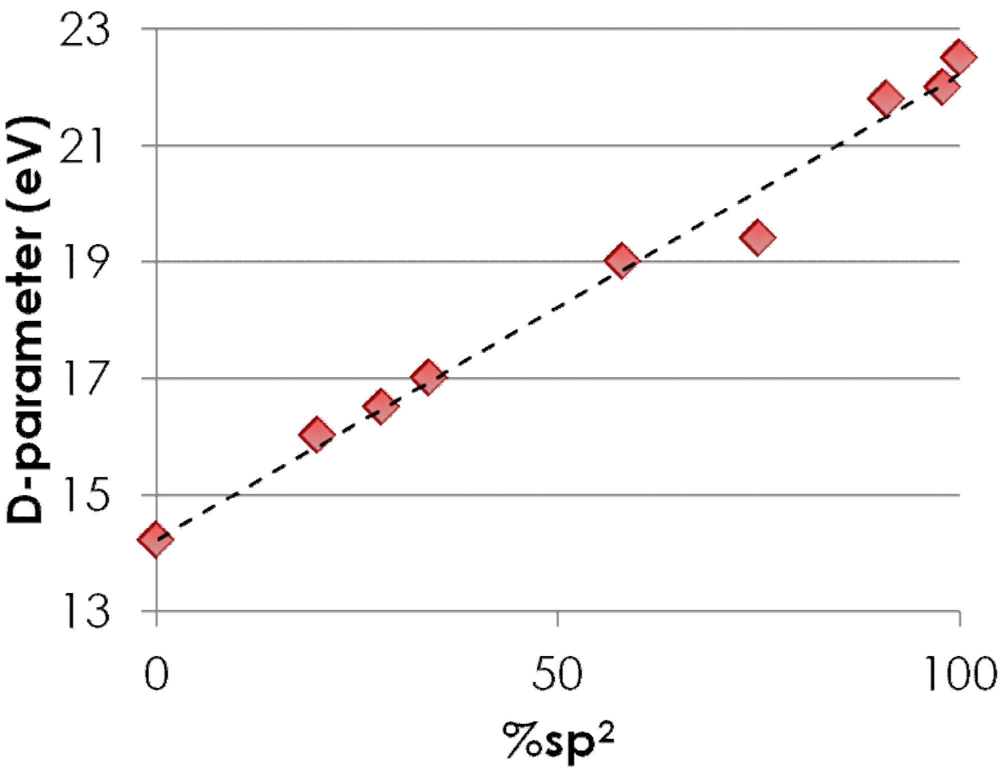
Surface bonding variation with particle size

Peak	I	II	III	IV	V
Binding energy range (eV)	284.3 - 284.5	285.1 - 285.5	285.6 – 286.5	287.0 – 287.8	288.1 – 288.8



Steer et al,(2015)The effects of particle grinding on the burnout and surface chemistry of coals in a drop tube furnace

sp^2/sp^3 carbon hybridisation using x-ray excited Carbon Auger electrons



Lascovich, Giorgio and Scaglione, (1991)

- The sp^2 percentage is estimated by a linear interpolation between diamond (100% sp^3) and graphite (100% sp^2) D values
- Comparison between raw coals and coal chars showed a higher percentage of sp^2 bonding for chars
- Smaller char particle size consistently had lower sp^2 character
- Highly ordered graphitic (sp^2) bonding has been correlated with lower char reactivity

Summary

- XPS allows the collection of both photoelectrons and auger electrons
- XPS can provide a range of chemical information including elemental, bonding, and imaging information
- My future work using XPS will investigate char reactivity variations with regards to particle size fractions, volatiles, and char residence times

The use of x-ray photoelectron spectroscopy for coal characterisation

Dane Sexton
PhD Student
Cardiff University School of Engineering

Supervisors: Dr. Richard Marsh, Dr. Julian Steer

Coal analysis and operability in iron and steel