KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY

NEWS 05 2021

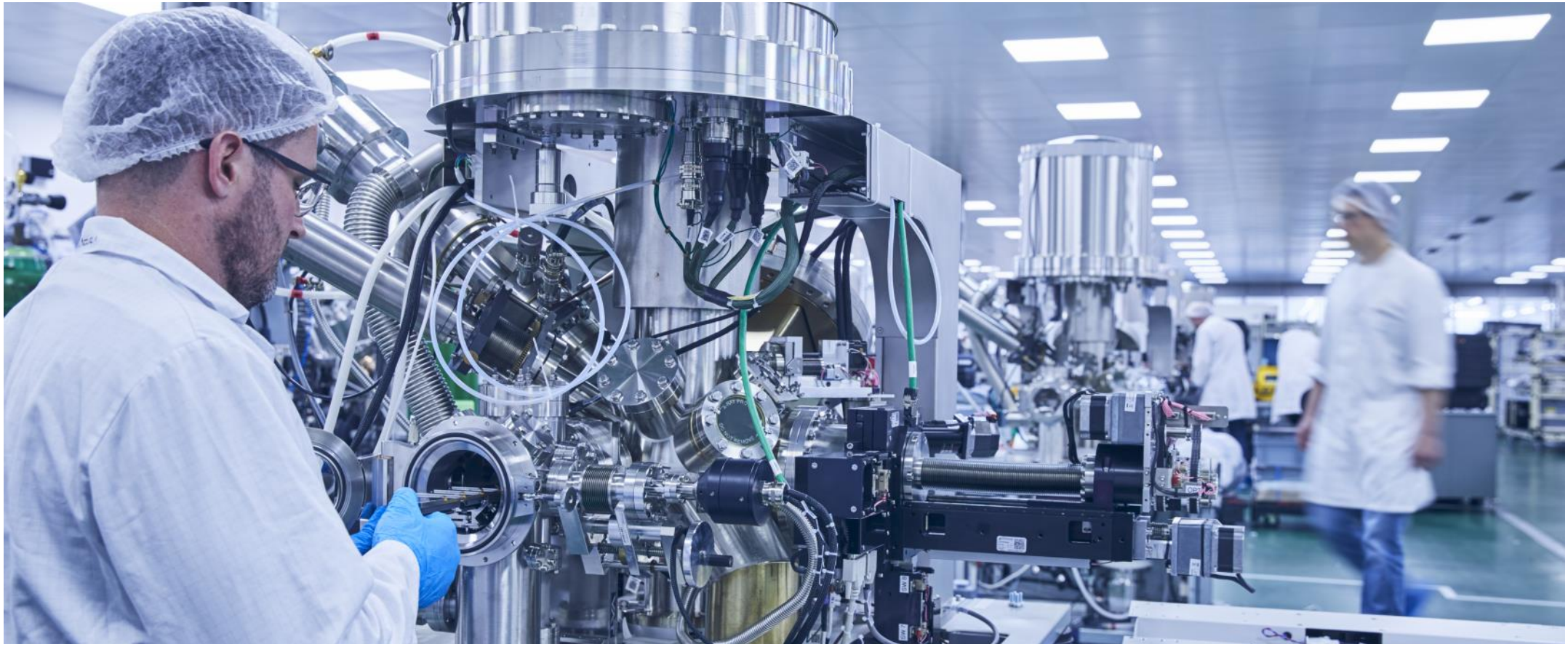
Tips, Tricks & Thoughts from the Apps. Lab.
A little of what we know

i-work
Interview with an employee

XPS in the UK : past & present
Standing on the shoulders of giants

Meet our Users
Dr. James McGettrick

Looking back at development of Kratos spectrometers
XPS for the 21st century



WELCOME TO THE SUMMER KRATOS NEWSLETTER

Surface analysis in the UK

It is with great sadness that we have learned of the death of Dr Martin Seah MBE in early June. During his career at NPL he pioneered metrology for surface chemical analysis. Martin began his career at NPL in the same year that Kratos sold its first instrument to Durham University.

Later in the newsletter we highlight the development of the technique and Kratos' contribution, supplying numerous instruments to academic and industrial labs in the UK over the last fifty-plus years.

The theme of *surface analysis in the UK* is continued in our User interview with Dr James McGettrick from Swansea University, where we discover the diverse range of samples analysed and the importance of surface characterisation of modern materials.

The i-work interview is with Kratos' Software Manager for the Surface group. We learn something of the challenges and motivations of writing software for complex analytical instruments.

We also have our regular Tips, Tricks and Thoughts from the Applications lab.

Enjoy the read.

info@kratos.co.uk

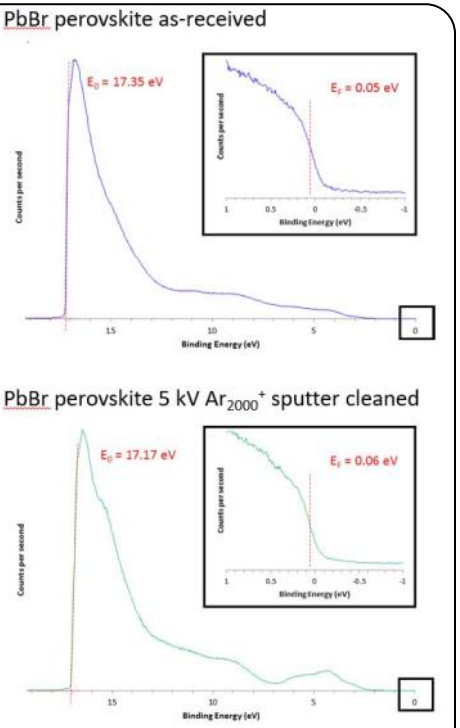
www.kratos.com

TIPS, TRICKS AND THOUGHTS FROM THE APPLICATIONS LAB.

We hope to give some insights into things that we do in the applications lab that might help our Users in their data acquisition and processing. If you'd like to share any of your own advice with our User community, why not contact us and we'll publish the best of them.

Ultraviolet photoelectron spectroscopy

We've seen a lot more requests for ultraviolet photoelectron spectroscopy (UPS) data over the last 18—24 months. This has been mirrored by an increase in instruments sold with the UV-lamp accessory. It appears that the increasing popularity of UPS is driven by the capability to determine the work function of the material being analysed. UPS also provides information on the energy position of the valence band maximum and the density of states at the Fermi level. Understanding the electronic structure of materials used in photovoltaics, batteries and power storage devices is vital to their successful application.



Effect of GCIS sputter clean on UPS spectra acquired from hybrid organic-inorganic PbBr perovskite. From applications note MO456(A)

It's important to remember that the kinetic energy of the UV-excited photoelectrons is much lower than those excited by conventional Al Kα X-rays. As a consequence the sampling depth of UPS is less than XPS, in other words UPS is more surface sensitive. This means that UPS measurements are much more affected by surface contamination.

A successful approach used in the Manchester applications lab is to remove surface contamination by sputter cleaning the sample. Note, that we differentiate between sputter cleaning and sputter profiling. The motivation of sputter cleaning is to remove surface contamination without changing the chemistry or stoichiometry of the material. This is only possible with a gas cluster ion source using large clusters of low energy. Our standard GCIS sample cleaning mode is 5 keV Ar_{2000}^+, where the partition energy (energy per Ar atom) in this mode is 2.5 eV. Such low projectile energies are not possible to achieve using monatomic Ar^+ ions.

It is worth commenting further that removing the surface contamination from the material might change the measured work function, with the value determined for the sputter cleaned sample being more representative of the material itself. It is recommended that the work function of the material is measured before and after sputter cleaning.

The ability to combine low energy, cluster ion cleaning with UPS has proved extremely useful in generating the best possible data from samples.

German Users' Meeting

We held our German Users' Meeting over two afternoons at the end of May. The meeting was held in German and one of it's unique features was that every attendee provided an overview of their institute and the research that their Kratos spectrometer has contributed to in the preceding 24 months. We had over 30 attendees from 17 different institutes, demonstrating the depth and strength of the German Kratos User community. For any User interested, the majority of the presentations are available in the Members Area of our website.

If you are interested in organising a local meeting in your country, please let us know as we'd be happy to support similar local meetings.

Other ways to keep in

contact with Kratos

Have you joined our LinkedIn community? Kratos Analytical already has over 2,300 followers. We post regularly with articles and updates on recent activities. It's also an ideal platform to highlight your published papers to share the great data generated using Kratos spectrometers.

As mentioned above, we also have a dedicated Members Area on our website, where you must have a login assigned for access. One of the primary uses of this restricted area is the distribution of the latest version of the ESCApe software.

Why not create a new Members account or login and see what's new?

i-work

Interview with an employee

Name Jay Chippendale

Job title Surface Science Software Manager

How would you describe your job to a 5-year-old?

My job at Kratos is to help design, write and test the software that is used to control our XPS instruments. I look after a team of software developers who write the code that makes the software work. Sometimes we get to use the instruments – but only if we promise not to break them with our software!

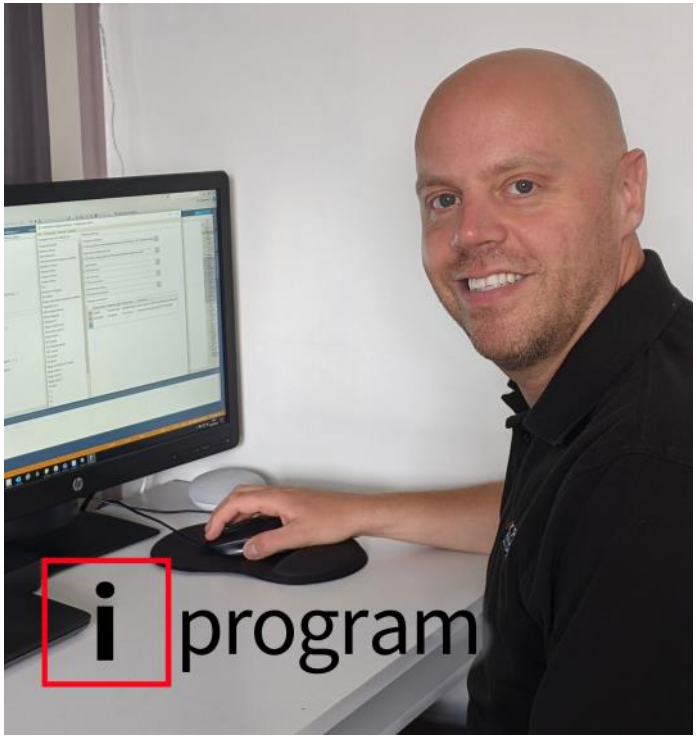
Best part of your job?

Some jobs in software can be very dull, writing code for back-end servers and such-like where you never get to see the end product. At Kratos working as part of a multi-disciplinary team with input from Mechanical Engineers, Physicists, Apps Specialists and so on, I'm involved in science that I would not naturally be drawn to. I get to see the end product and have to know every part of the system, from the firmware that sits just above the electronics, understanding the control of the instrument all the way up to the User interface via the ESCApe application, and presenting the data acquired from the instrument. Obviously, we can't just throw the data at the User, it has to be presented in it a way that is meaningful and allows them to understand their samples.

Another highlight is interacting with and helping our Users such as Samsung and Intel, big brand names.

How did you end up at Kratos? Your background/experience?

I did a degree in Computer Science and Mathematics at Keele University. After my degree, I wasn't sure where I'd end up working but during the interview at Kratos I was taken around the applications lab. Although the instruments were all quite abstract, they really caught my imagination and the idea that I could be writing software to control these huge bits of kit was



really interesting. I started in the MALDI group, spending the first 10 years in that Business Group until I moved to the Surface Group. Along with a couple of colleagues, I moved over to write the Windows based software that became ESCApe.

What have you learnt working at Kratos?

If you stay in one job, it's important to make sure you're still learning. I think this is particularly important in software which is always changing. It's also important to have core skills which can easily be transferable to different roles. That really helped me moving from MALDI software to surface instrument software. There was a steep learning curve moving to the surface analysis group. The surface analysis instruments are a lot more complicated, with the possibility of multiple excitation sources, different ion guns, instrument acquisition modes… all these items must be controlled, and data acquired and processed. I like to think that I have a good understanding of most aspects of the instruments but know there's always more to learn!

Being Manager of the software team, I've learned that I have to use the skills of the individuals where they're best suited. I must rely on their expertise, whether it's lower level device communication, databases, complex mathematical algorithms or User Interface coding for example, ensures that the individual contributions to the complete software solution is the best it can be.

Your favourite quote / line from a film or book?

"We choose to go to the Moon in this decade and do the other things, not because they are easy, but because they are hard"

What is your motto or personal mantra?

From the Agile manifesto that outlines the principles of best software practice; "Build projects around motivated individuals. Give them the environment and support they need and trust them to get the job done". It's a bit software related, but a good working motto.

Travels restrictions are lifted – where would you go?

Back to Santorini where I got married.

What keeps you busy when you're not at work?

My very active and busy 6-year-old son. My role does seem to be the dad-taxi, but I do enjoy watching him play football and cricket. When given the chance, I like to get out in the surrounding countryside on my bike and have been known to compete in the odd triathlon!

Tell us one thing that we don't know about you?

I once watched a film with Tyson Fury! It was before he was properly famous, but I quite like boxing so when he walked into the cinema I recognised him straight away. He sat next to me, so I leaned over and struck up a bit of a conversation. I asked him what his aim was in his boxing career and he said 'I want to go to the top, I think I'm good enough.' Turns out he wasn't wrong!

XPS in the UK : past & present

Standing on the shoulders of giants.

In 1969, AEI Scientific Apparatus Ltd (later Kratos Ltd) sold its first photoelectron spectrometer to Dr. David Clark's group at the University of Durham. The 1960's had seen the emergence of UHV technologies as many Universities were looking to exploit this new capability. At the same time, Vacuum Generators (VG) Ltd was formed in East Grinstead with a single product, an all metal right angled valve. Rapid growth of VG's business in the 70's led to the development of the ESCA lab, Auger and LEED instruments. In the following decades both Kratos and VG became established, UK based, global suppliers of XPS instruments.

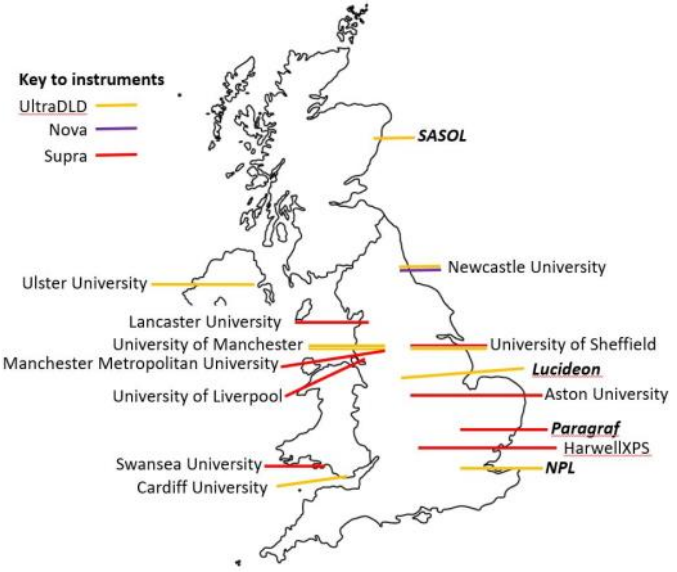
Although Kai Siegbahn had invented the technique of XPS in Uppsala, Sweden, it was the UK manufacturers that successfully commercialised it. Fast forward to the present day and VG is now owned by American instrument manufacturer, Thermo Fischer Scientific, and Kratos is a wholly owned subsidiary of the Japanese analytical instrument manufacturer, Shimadzu Corporation. Uniquely, Kratos Analytical continues to develop, build, sell, and support surface analysis instruments from its UK headquarters in Manchester.

There was considerable demand for photoelectron spectrometers, with over 30 Kratos ES100 instruments installed in laboratories throughout the world by 1972. The surface of solid materials had been little studied up to this point in time. UK industries identified the value that XPS results could add to their products. ICI were early adopters of the technique, sponsoring the PhD of a young David Briggs in the Durham University ESCA Group, exploring inorganic and catalytic systems using ESCA. After his PhD Dave Briggs understood the opportunities to apply knowledge of surface chemistries identified by XPS to commercially important ICI products. He moved to a research scientist position at ICI, Runcorn and there he obtained the next generation Kratos ES200 photoelectron spectrometer. Many other industrial labs in the UK were also keen to exploit the capabilities and results of this newly developed technique, including British Petroleum (Sunbury on Thames), UK Atomic Energy Authority (Warrington), Shell Research (Thornton, Cheshire) and Gillette Industries (Reading).

Whilst the 1970's saw XPS instruments being used in industrial labs, UK academia was also embracing the technique. The group at the University of Durham added a Kratos ES300 to their lab. Other ES-range spectrometers were installed in University of Oxford, University of Newcastle, University of Liverpool and UMIST. It's perhaps testament to the longevity of these instruments that a number of them were still being used when current Kratos employees were studying for their PhDs in the 1990's.

Both Kratos and VG continued to develop photoelectron spectrometers in the 1980s and 1990's. Kratos launched the XSAM and then the AXIS spectrometers, while VG sold their ESCALab instruments. Whilst UK instrument manufacturers were developing the hardware, important contributions to the interpretation of the data and standardisation were also being made. In this respect, we must recognise the contribution of Martin Seah who started his career at the National Physical Laboratory in 1969. Martin's colleague, Prof. Ian Gilmore, notes 'Martin realised, ahead of everybody that for such measurements to be of lasting utility in both research and industrial applications alike, rigour had to be introduced to this new discipline of surface chemical analysis. He led a metrology campaign to ensure measurements in industry were fit-for-purpose and reliable.' Indeed, Kratos Business Manager, Dr. Chris Blomfield acknowledged that 'Martin transformed the technique from unreliable and semi-quantitative to a routine analytical technique used in industry and academia around the world'.

Moving into the 21st Century both Dave Briggs and Martin Seah were instrumental in selecting Kratos AXIS spectrometers for their labs. Dave was a Professor in the School of Pharmacy at the University of Nottingham and Martin then a Senior NPL Fellow. The latest generation of AXIS Supra and AXIS Supra^{+} spectrometers are well represented in UK academia. Further improvements in sensitivity and resolution as well as unrivalled automation ensure that our spectrometers are contributing to results published from leading universities in Manchester, Lancaster, Liverpool, Aston (Birmingham), Sheffield and Swansea. Modern spectrometers can also boast the addition of gas cluster ion sources, facilitating the successful sputter depth profiling of organic materials, technology that was in part developed by John Vickerman and colleagues at the University of Manchester.



The use modern XPS spectrometers is perfectly demonstrated in reviewing data provided by Dr. Dave Morgan from the EPSRC National Facility for X-ray photoelectron spectroscopy, HarwellXPS. The facility is equipped with both a Kratos and Thermo instrument. Dave comments that there are over 180 individual Users of the facility from 46 UK universities and 6 industrial research groups. Interestingly, the most analysed class of samples at HarwellXPS are catalysts, one of the first types of materials studied in the pioneering work at the University of Durham. We conclude that, over 50 years after the first commercial instrument was installed, XPS and surface analysis still underpins much of the UK's materials surface characterisation.

MEET OUR USERS

Dr. James McGettrick : SPECIFIC Project, Faculty of Science & Engineering, Swansea University

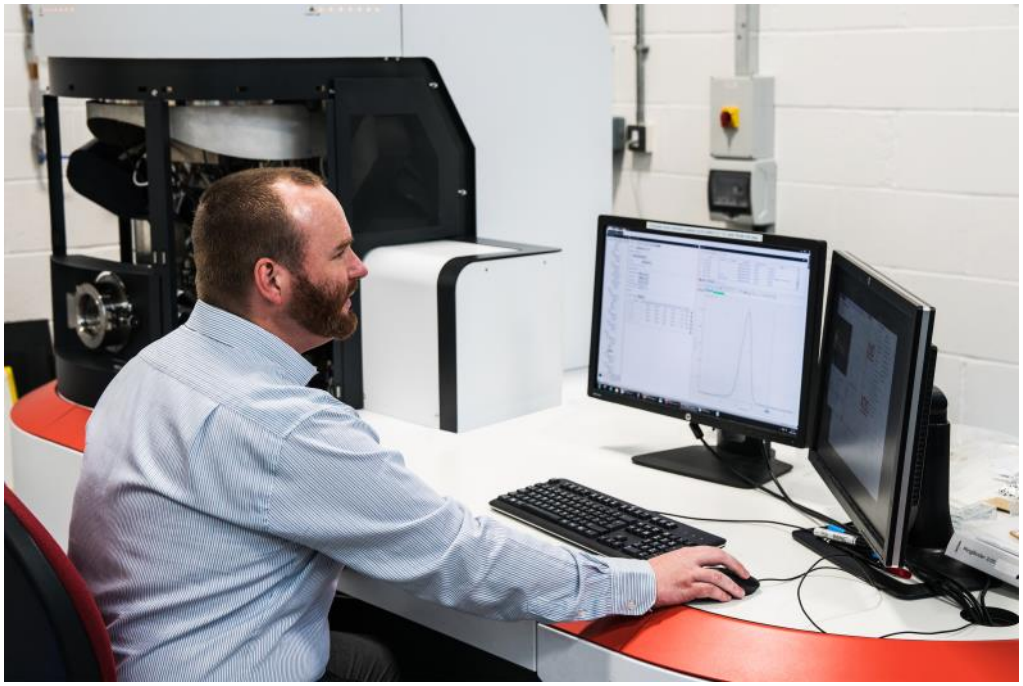
What is your role at Swansea University?
Technology Transfer Fellow .

Can you describe a typical day at work?

It depends a little on the day of the week. In midweek the XPS is open to bookings from across the University, so I will always call in on the XPS lab first thing to check on the current user. This can be a fun casual chat with experienced users, but with less experienced users it can end up with an hour or two discussing their experiments. For instance, last week a relatively inexperienced user was showing me "chemical shifts" on Zn(2p), so I had to explain ways to spot differential charging & discuss how set up the experiments more carefully.

I tend to use the XPS for my own work on Thursdays or Fridays so that I can run an anti-socially large amount of experiments and depth profiles over the weekend. Those days can be very busy as we often try to make samples in wet chemistry labs in the morning and run the XPS the same day. We do a lot of work with perovskite photovoltaics – multilayer devices from relatively simple processes. These materials *can* be very stable, but this is not always true when production processes are varied, and as our group specialises in scale-up work we *must* vary production processes.

Once the samples are in the XPS it's usually a very convenient time for lunch (on the beach on a sunny day – we're very lucky with our campus location), emails and other bureaucracy. When you return to the instrument in the afternoon, you'll have a lovely set of auto-Z and wide scans that you can use to build your overnight queue.



How do you use your Kratos instrument in your role?

My boss said one thing to me when we bought the XPS in Swansea: "This has to be something that we can use for everyone in the University" and the range of samples reflects this: bone, corroding power cables, rocks, catalysts.

Although I'm the primary user, we believe in trying to get as many users as practical operating the XPS – we've had about 28 so far, with the main limit being instrument time. This approach has pros and cons. It's a core part of our role as a university to impart technical skills to our students where we can, but it does take time and accidents can happen. Usually this is trivial – the TEM grids on sample bars do not survive contact with students for long – but sometimes more time consuming.

In terms of the instrument itself, it runs 24/7 with surface spectra primarily during the week and depth profiles running most weekends. Whilst my own work focuses on photovoltaic materials – perovskite, OPV and semi-conducting materials in particular – we're part of a Materials Engineering department with a strong history of working with steel and studying the electrochemistry of corrosion. Corrosion can make surface analysis complex with multiple unknown species present and the surface being a mix of conductor, semi-conductor, and insulator.

Why do you think XPS and surface analysis important in materials development?

I just think that you're missing a huge piece of the puzzle in any modern product if you don't understand the various layers and interfaces within it. The steel products that I focused on early in my career and photovoltaics we look at now can suffer many of the same problems. Poor adhesion or wetting can destroy your product or store away an early failure once in use. Contamination or unwanted by-products are something that you don't want in any production process and that's before you even think about the difficulty of analysing single molecules or sub 100 nm layers by other techniques.

What has surface analysis taught you?

Patience and a scepticism.

More seriously it's more what surface *analysts* have taught me. I've been lucky with mentors over the years. Wayne Schofield in Durham, and then Tim English and Debbie Hammond (now running Sheffield's Supra) at Corus/Tata Steel. Surface analysis isn't something that can exist in a vacuum (bad pun intended). We have the most impact when we understand the whole sample history and can contribute to a wider team. We also need to be able to explain your work in a way that is helpful to the audience – and understand what's important to them. Whilst modelling every peak on a spectrum is sometimes interesting to me, it isn't needed for everyone.

Any tips or tricks for surface analysts?

Listen to the Kratos team – I have been sceptical at times about some of their suggestions and they've always been correct. Probably their most helpful advice was to float everything when charge neutralisation get tricky. It's not magic, but it does work 99% of the time.

How we arrived at the AXIS Supra$^+$: XPS for the 21st century

Our recent poll on LinkedIn asked 'If you had to choose, which resolution do you consider most important for your surface analysis instrument; energy (spectroscopic) or lateral (imaging and small spot)? The answer was overwhelmingly 'energy' with 85% of the vote. Interestingly, one person used the comments to suggest 'both', and if I were looking to purchase a new spectrometer I'd probably be inclined to agree. I suspect that the responses to the poll reflect the primary use of the spectrometer. Where energy resolution is most important, the instrument is considered a spectrometer, providing spectra from samples to characterise quantitative surface chemistry. For the 15% that voted lateral resolution as more important, perhaps the instrument is considered as a microscope, providing images of the distribution of elements or chemistry at the surface as its primary role.

Kratos spectrometers have always been designed to achieve the best possible energy resolution in spectroscopy mode as well as providing excellent lateral resolution in small spot spectroscopy and XPS imaging modes. With an AXIS instrument you get the best of both worlds!

Development of our spectrometers, from the earliest ES-series through the XSAMs to the AXIS instruments, has been guided by the fundamental requirement for the best energy *and* lateral resolution.

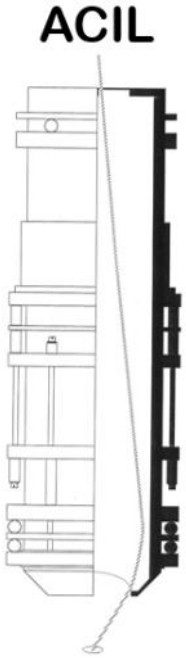
An early improvement in spectroscopic performance was achieved with the use of a monochromatic X-ray source. This is easily demonstrated by considering the full width at half maximum of the Ag $3d_{5/2}$ peak under the same instrument acquisition parameters.

Excitation source	Ag $3d_{5/2}$ FWHM
Al Kα achromatic	0.80 eV
Al Kα monochromatic	0.48 eV

Because the energy dispersion of the monochromator is inversely proportional to its diameter, with this component of the spectrometer, bigger is better. The use of a large, 500 mm diameter Rowland circle monochromator on Kratos instruments ensures that there is less energy dispersion in the X-ray illuminated area at the analysis position, contributing to higher energy resolution.

The electron optics (transfer of the photoelectrons from the sample to the hemispherical analyser) also contribute to the energy resolution of the instrument. The inclusion of slits/ apertures in the lens column and entrance to the hemispherical analyser improve the energy resolution in spectroscopy mode by decreasing the energy spread and scattering of the photoelectrons. The slot aperture used to collect large area spectra is specifically configured to collect fewer electrons in the energy dispersive direction of the mono-illuminated area than the non-dispersive direction.

The aberration corrected input lens (ACIL) was introduced with the XSAM series spectrometers and a variant of this lens continues to be used in the latest generation AXIS Supra$^+$ instrument. Aberration correction is fundamentally important for ensuring good spectral energy resolution for electrons collected from a large solid angle. By inserting an aperture into the lens column and simultaneously closing the angle-defining iris, the ACIL may be used to define a small, selected area from which the photoelectrons are collected.



Further development of the ACIL led naturally to the introduction of a scanning system as foreseen in the original ACIL patent. XPS maps were acquired by rastering the collection area of the photoelectrons across the surface of the sample. This was the advent of spatially keyed spectroscopy, where an area of interest is identified from a map of the lateral distribution of an element. With the development of the ACIL, lateral resolution of XPS became important.

A step-change in imaging mode lateral resolution was made with the development of the AXIS Ultra, which combined a modified ACIL with a magnetic lens and the Kratos patented spherical mirror analyser (SMA). When introduced, this combination of electron optics and SMA allowed stigmatic, also known as parallel imaging, with a spatial resolution specification of 3 µm. The current generation AXIS Supra$^+$ boasts 1 µm ultimate resolution when operated at the highest imaging magnification.

Properties of the SMA mean that it can be operated at high magnification with high transmission and low spherical aberration (distortion). Furthermore, this imaging analyser operates in fixed analyser transmission (FAT) mode, just the same as the HSA for spectroscopy mode. This means that images not only have high spatial resolution but, by selecting lower pass energies, can also have high energy resolution.

So, whether energy or lateral resolution is of primary importance, whether your requirement is to acquire high energy resolution spectra or well resolved high magnification images, a modern XPS instrument should excel at both.