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This is the Vacuum Generators model 220iXL X-ray photoelectron spectrometer at INRS-ÉMT. The metallic dome on top is the electron spectrometer (hemispherical analyzer), connected to the analysis chamber below it by a long tube containing the electron lenses and apertures. The analysis chamber and housing for the hemispherical analyzer are formed from mu-metal (77% Ni, 15% Fe, plus Cu and Mo), an alloy which screens out external magnetic fields. The analysis chamber is connected to a stainless steel preparation chamber at right, which has the shape of an oblate sphere and which is whimsically called an R2P3 chamber by the manufacturer (but not by us.) The preparation chamber houses a rotating arm on a translation mechanism that is used to deliver the sample to the analysis chamber or to any of the ports and stations on the preparation chamber. Projecting from the front of the preparation chamber is the fast-entry air lock, a small, independently pumped chamber that is the only part of the vacuum system that is let up to air during normal operations. Bolted onto the preparation chamber at right we can see a custom-made electrolytic cell used by Daniel Guay and his collaborators for the deposition of catalytic thin films. Because these films are air-sensitive, the custom chamber has been connected to the spectrometer to allow the transfer of samples for analysis under vacuum. Behind the spectrometer we see gas bottles containing dry nitrogen for venting the air lock to air, argon for the ion gun and helium for the UV lamp.
The operator sits at the left of the instrument in front of the valve controls, the vacuum gauges and controls for the electron flood gun, ion gun and UV lamp. He has a small monochrome television to see his sample inside the analyzer chamber, a large colour monitor for XPS imaging, and a PC for controlling the spectrometer functions. At right we see the manual controls for the motorized sample stage.
The video camera, occupying a fixed position on the analysis chamber, is focussed on the point in space “seen” by the analyzer optics, allowing the sample position to be easily adjusted and the point of analysis to be visually identified; essentially, it will be the point in focus under the cross-hairs on the TV monitor.

Behind the camera, a Faraday cup will give a rough secondary electron image from the electron flood gun, which can be useful in positioning the sample for imaging XPS.
The VG Eclipse data acquisition and analysis software runs on OS/2, a 32-bit multitasking operating system that never really caught on. We generally use Eclipse just for data acquisition and then do the data analysis offline with CasaXPS, a third party software application that runs under windows.

http://www.casaxps.com
At the right of the instrument sits the panel for controlling the X-ray sources. The power supplies for the monochromated source are on top, with the supplies for the non-monochromated "twin" source underneath. These supplies provide up to 15kV to the X-ray guns.
The electron spectrometer, a hemispherical analyzer device, sits above the analyzer chamber. Two viewports shielded with high-lead glass are provided for direct visual inspection of the interior of the vacuum vessel, and are mostly needed during the transfer of samples into and out of the chamber. Many additional ports are located at various angles and orientations around the spherical analysis chamber. The chamber itself is constructed from two welded hemispheres blown in mu-metal, a somewhat soft alloy, necessitating some caution regarding the stresses placed upon the ports.

The vacuum in the analysis chamber is maintained by an ion pump at something (hopefully) close to $10^{-10}$ mbar. The pumping characteristics of an ion pump are a little delicate but it has the advantage of being sealed and not requiring evacuation by a secondary pump. This means that in the case of a power cut, there is no risk of contaminating the analysis chamber with pump oil.
The preparation chamber houses a sample transfer mechanism, basically an extendable arm on a pivot. It can be wound into the fast entry air lock, once the gate valve separating the air lock and the preparation chamber has been opened, which itself requires a good vacuum in the air lock. There the sample clips onto the end of the arm, which is then retracted. Once fully retracted, the arm can be rotated about its central pivot in order to point towards one of the eight equatorial ports on the chamber (including the gate valve separating the preparation and analysis chambers.) A multitude of ports is provided on the chamber in order to facilitate the addition of preparation devices and vessels.

The vacuum in the preparation chamber is maintained at about 5x10⁻⁹ mbar by a magnetic levitation turbomolecular pump.

The operation of the valves separating the analysis chamber from the preparation chamber, and the preparation chamber from the fast-entry air lock, is overseen by a logic circuit that prevents the accidental contamination of the system by air.
The fast-entry air lock encloses a much smaller volume and is pumped by a small turbomolecular pump. The air lock door houses a fork onto which the sample holder is plugged, ready for capture by the mechanism at the end of the transfer arm in the preparation chamber. The FEAL is let up to atmospheric pressure with dry nitrogen and for as short a period as is necessary to put the sample holder into place. The vacuum in the FEAL is not measured directly but is probably in the $10^{-6} - 10^{-7}$ mbar range during sample transfer to the preparation chamber. The logic circuit controlling the valve operations uses the rotation speed of the small turbomolecular pump as its criterion for the safe opening of the gate valve leading to the preparation chamber.
The twin-anode non-monochromated X-ray gun sits between the Faraday cup and the bell-jar housing for the monochromated X-ray source. The cooling water and high-tension supply come in through the metallic hose emanating from the top of the gun, with the filament supplies coming in from the side. The gun sits on a linear transfer mechanism that allows it to be set closer to, or further away from the sample. When not in use, the gun is retracted to afford greater room for manoeuvre in the analysis chamber, and it is wound in when in use in order to maximise the X-ray flux on the sample.
Looking through the porthole we can see the nose of the X-ray gun next to the sample.
The nose of the X-ray gun is the copper tube coming in from the 10 o’clock position. The sample (a polymer film on a coupon of glass) is affixed to the sample holder, which sits at the end of the rectangular copper sample manipulator coming in from the 8 o’clock position.

The steel tube coming in from 11 o’clock contains the optics for the TV camera. The copper tube coming in from 12 o’clock is the entrance to the analyzer lens stack. At the 2 o’clock position we see the port and gate valve leading to the preparation chamber.

The large metal stub underneath the sample is the magnetic immersion lens, which produces a magnetic field that guides a greater proportion of the photoelectrons into the analyzer acceptance cone without changing their energies. The magnetic “XL” lens effectively doubles the analyzer acceptance angle for routine work and can improve the signal by a factor of 10 for the more extreme “small area analysis” lens programs.
At bottom right we see inside the X-Ray source. The high tension accelerates electrons from the filament onto one of the anode faces, made of copper (to facilitate heat dissipation) covered with a thin film of the anode material, either Al or Mg. The energetic electrons knock out electrons from core orbitals in the target atoms (upper left) to create core holes. An electron from an upper orbital drops down to fill the hole, and in doing so, emits an X-ray photon carrying away the excess energy. Because the metal 2p level is split, the main peak in the X-ray spectrum is a non-resolvable doublet called the K\(_{\alpha1,2}\) line (upper right.) In non-monochromated X-radiation, this line is accompanied by smaller satellite lines and a continuous Bremsstrahlung background due to decelerating electrons (lower left).
Accompanying the Kα₁,₂ line and the Bremsstrahlung are a series of satellite lines that cause small peaks in the XPS spectrum at set intervals and relative intensities with respect to the principal photoelectron peak. Certain satellites are due to alternative transitions that fill the core hole (the Kβ line is due to a transition from the valence band) while others are due to emission from doubly ionized atoms (e.g. Kα₃,₄).

Also listed in the table above are the positions of “ghost” satellites that arise if the X-ray source anode is on its last legs. XPS peaks produced by O Kα radiation originate from oxidized anodes while peaks produced by Cu Lα radiation arise from worn anodes with holes in the Al or Mg thin film.
Most XPS users prefer to work with a monochromated Al X-ray source. It uses quartz crystals glued onto a curved support in order to provide some degree of focussing. The first order reflection provides monochromatic radiation from an Al target, the X-ray line width being reduced from the natural 0.85 eV for the Kα\textsubscript{1,2} doublet to ~0.26 eV. The result is a noticeable improvement in spectral resolution and the elimination of X-ray satellites. Although the X-ray flux density on the sample is about the same as for a non-monochromatized source (4-6x10\textsuperscript{11} photons mm\textsuperscript{-2} s\textsuperscript{-1}) the Bremsstrahlung has been stripped away and less damage is done to fragile samples like polymers.

The X-ray monochromator sits in a bell-jar housing at the back of the analysis chamber. Inside the top of the bell jar sit the two bent quartz crystals. Micrometer screws projecting from the top of the bell jar allow the alignment of these crystals to be fine-tuned.
The monochromated X-ray source on our instrument is of a design acquired by VG from Surface Science Laboratories Inc., and features the possibility to focus the 10keV electron beam onto the surface of the Al-covered anode. In this way, the size of the X-ray footprint on the sample may be varied between 150 µm and 1 mm. This capability, combined with the selection of “small area” lens modes available in the analyzer, affords a high degree of flexibility in the targeting of specific surface features on the sample.

There are two main disadvantages associated with monochromated X-ray sources. First, the Bragg geometry requires the X-ray anode, quartz crystals and the sample under analysis to sit on a Rowland circle, so that the sample has to be carefully positioned at the focal plane of the monochromator. Second, specific action needs to be taken to correct the accumulation of charge at the surface of insulating samples. A non-monochromated source illuminates the sample with low-energy electrons produced from the aluminium foil window in the nose of the gun, so that charge compensation is essentially automatic and fairly uniform. The monochromated source, on the other hand, does not emit enough electrons to compensate for the departure of photoelectrons from an insulating surface.
Most X-ray photoelectron spectrometers these days use a hemispherical analyzer. In general, the bigger the hemisphere, the better.
It consists of a pair of concentric hemispheres. The inner hemisphere is biased positive with respect to the outer hemisphere so that electrons entering the analyzer are forced to follow a curved path in the analyzer to reach the detector. The analyzer “pass energy” is the energy of those electrons that follow a path along the curve described by the average radius \( r_0 = \frac{r_1 \cdot r_2}{2} \). If the pass energy \( E_0 = eV_0 \), then voltage between the hemispheres is

\[
V_2 - V_1 = V_0 \left( \frac{r_2 - r_1}{r_1 - r_2} \right)
\]

Typically, a pass energy of 100 eV will be employed for the acquisition of survey scans, in which signal intensity counts more than spectral resolution. For high-resolution scans of individual peaks, the pass energy will be set to 20 eV, for which the signal intensity is lower but the resolution better.

The hemispherical analyzer has energy dispersive properties that can be utilized by multichannel detectors to sample several points in the spectrum simultaneously.
The hemispherical analyzer is normally operated with a fixed pass energy for a given spectrum in XPS (constant analyzer energy CAE, or fixed analyzer transmission FAT, mode) so in order to scan the energy scale the electron retardation is done in the lens stack in front of the HSA. A number of lens programs are selectable in the operating software depending upon the type of analysis required. Typically the “large area electrostatic” or “large area XL” (the latter employing the magnetic lens) programs are used for routine analysis. Using the non-monochromated X-ray source, the area analyzed using the “large area electrostatic” lens program is 2 mm x 3 mm in size. Various “small area” lenses are also provided, with the minimum analysis area on our system being a circle 20 µm in diameter.

There is also an imaging mode available which essentially projects an image of the photoelectrons emerging with a given energy from a selectable surface area between 150 µm and 8 mm in diameter onto a 2-dimensional channelplate detector. XPS imaging is a rapidly developing field that I propose to ignore completely in this presentation.
The detector array sits at the back end of the hemispherical analyzer.
Our array is equipped with six channel electron multipliers (channeltrons; b) for spectrum acquisition and a channelplate (c) for photoelectron imaging. The channeltron is essentially a miniature glass horn coated with an electron-emissive material that when struck by electrons, emits even more electrons. A 2-4 kV potential difference applied between the input cone and the end of the device, combined with the curved shape which ensures that emitted electrons strike the coating further up the voltage gradient, allows for the multiplication and subsequent detection of an incoming photoelectron current.
The channeltrons are distributed along the energy-dispersive direction of the analyzer in order so sample the spectrum at six points simultaneously. The output of these channeltrons is then summed, taking into account the energy interval between them, in order to increase the sensitivity of the instrument.

The detector array pictured above comes from a Kratos Axis Ultra instrument, and has eight channeltrons.
The X-rays striking the sample are neutral particles and the photoelectrons emitted carry a negative charge, so the sample surface will have a tendency to acquire a positive charge. This tendency will be realized in insulating samples, and measures must be taken to compensate for the charge build-up. A common method of charge compensation is to flood the sample surface with low-energy (0-10 eV) electrons, while hoping that no electron stimulated desorption of material occurs.

The non-monochromated "twin anode" X-ray source has an ultrathin aluminium window in the nose to prevent stray electrons from the filament from reaching the sample, and the passage of X-radiation through the window produces a reasonably uniform flux of low-energy electrons that accomplishes the task of charge compensation. The spectral peaks generally do show a shift due to residual charging of a few eV but the charging is not severe enough to degrade the quality of the spectrum.

The monochromated source also has an aluminium window but it is much further from the sample. For the analysis of insulators, it is necessary to use an electron flood gun in combination with the monochromated source.
The electron flood gun is little more than a filament placed on the nose of the analyzer lens stack. The filament current and electron energy are the principle characteristics selectable on the controller. The electron gun is able to operate both in the low energy (0-12 eV) flood regime and also in a higher energy regime (500 eV) designed for charge compensation during SIMS analyses and for electron imaging, useful when aligning the sample for photoelectron imaging.
An attempt to analyze an insulating sample with monochromated X-radiation and no charge compensation will result in a completely degraded spectrum (a).

Flooding the sample with low energy electrons (b) will compensate for the accumulation of charge due to photoelectron emission. However, the characteristics of the charge compensation (chiefly the flux and energy of the electrons provided) can be optimized to either place the photoelectron peaks at the "correct" energies in the spectrum or to minimize the peak widths, but usually not both simultaneously. Most users prefer to minimize the peak widths experimentally (c) and to perform the peak energy correction in software.
The goal is to ensure a uniformly low level of residual charging across the entire X-ray footprint. This can be tricky in the case of an analysis with a small beam of monochromatic X-rays, because the area around the X-ray footprint will have a tendency to charge more negative than the X-ray footprint itself, which may result in the reflection of low-energy electrons from the analyzed area. One way to avoid the build-up of excess negative charge around the analysis area is to place a grounded washer on the sample and perform the analysis on the surface showing through the hole.
The left side of part (a) of the figure illustrates photoemission from a core orbital in a conducting sample. The entire photon energy is imparted to the photoelectron in this case, which “pays” its binding energy $E_{BE}$ plus the sample work function $\phi_s$ in order to escape into the spectrometer with a kinetic energy $KE_1$. In the detector, it will fall into the vacuum level $E_v$ of the analyzer and the kinetic energy measured will be $KE_2$. The work function $\phi_i$ of the instrument will have been determined, so the measured electron kinetic energy $KE_2$ can be corrected to the spectrometer Fermi level, giving the determined kinetic energy $E_{DET}$. Because the sample is a conductor, its Fermi level will have equilibrated with the spectrometer Fermi level if it has been put in proper electrical contact (my means of affixation to the sample holder with screws or conducting tape), and the corrected electron energy $E_{DET}$ can be directly related to the orbital binding energy $E_{BE}$ through the Einstein equation $E_{BE} = h\nu - E_{DET}$ without knowing the value of $\phi_i$.

The case for an insulator is more complex. It is not in electrical contact with the spectrometer and so its “Fermi level” will not align with that of the analyzer. In addition, the sample will acquire a potential that will be determined by the flooding electrons. The experimentally determined photoelectron energy $E_{DET}$ relates to the spectrometer Fermi level, which is itself related to the sample Fermi level through $E_e$, the energy of the flood electrons, and the sample work function $\phi_s$, both of which must be known in order to determine the orbital binding energy $E_{BE}$ absolutely.
The “magnetic lens” sits underneath the sample.
The idea is to guide emerging photoelectrons along the magnetic field lines into the analyzer lens stack. The magnetic field lines can also be used to guide low-energy electrons from a filament at the nose of the analyzer down onto the sample surface to assist in charge compensation. The efficiency of the charge compensation can be enhanced by the addition of a reflector plate as shown in order to maintain a cloud of low energy electrons in the vicinity of the sample surface.
Our instrument is also equipped with an argon ion gun. This device ionizes a small volume of argon gas at about $10^{-5}$ mbar by means of electron impact from a filament, extracts the positively charged ions through a grid held at negative potential and then accelerates, focuses and rasteres the ion beam.

The ion gun is used to clean the sample surface, if required, prior to analysis, or to erode the surface for the compilation of a composition depth profile. In principle, it can also be used for Ion Scattering Spectrometry if fed with helium, although I am not aware that anybody has done this in our laboratory.

The ion gun will deliver a rastered 100 $\mu$m diameter beam of argon ions at energies up to 5 keV and ion currents of up to 1 $\mu$A.
Here we see the nose of the ion gun coming in from the 2 o’clock position.
By alternating periods of ion beam erosion with periods of spectrum acquisition, a composition depth profile may be acquired. The erosion rate will depend upon the ion beam parameters and the sample composition, but it is common to refer back to an erosion rate determined under the same operating conditions on a tantalum oxide thin film standard, purchased from the Institute of Reference Materials and Measurements in Belgium.

http://www.npl.co.uk/npl/cmmt/sis/refmat.html#Tantalum

This is an example of depth profile information for the Ta4f and O1s peaks during just such a calibration on a 30 nm Ta2O5 film on Ta. The tantalum peaks are seen to shift from binding energies characteristic of the oxide to binding energies corresponding to the metal, and the oxygen peak is seen to disappear as the oxide-metal interface is reached.
Quantification of this data reveals an oxygen depth profile consistent with the oxide stoichiometry. Comparing the apparent position of the oxide-metal interface on the time axis with the known (and certified) oxide thickness, we determine an etch rate of $1 \text{ nm / min}$ in this material under the operating conditions employed.
Finishing the tour of the instrument, we come to the UV lamp used for valence-band studies (ultraviolet photoelectron spectroscopy, UPS). The device basically ignites a discharge in small volume of helium by the application of a voltage of somewhat less than 1kV. The helium plasma in the lamp emits UV light that is dominated by 21.2 eV (He I radiation) or 40.8 eV (He II radiation) photons, depending upon the gas pressure. Valence band orbitals have very large photoemission cross-sections for photons of such low energies.
Valence band spectra are characteristic of inter-atomic bonding in ways which core orbital spectra are not. For example, the XPS survey spectra of high density polyethylene and polypropylene are virtually identical, both polymers containing only carbon and hydrogen.
The C1s high-resolution spectra are similarly identical. The overall carbon valence electron density is similar in both polymers and core orbital effects are not able to distinguish between the two polymers.
The valence band spectra, however, are quite dissimilar, because these spectra are sensitive not only to the chemical composition of the sample but also to the manner in which its constituent atoms are arranged in space. Valence band spectra, therefore, even X-ray photoelectron spectra like these, are useful “fingerprinting” tools for chemically identical materials.

The detailed interpretation of the peaks in valence band spectra is usually attempted in concert with quantum chemical calculations of the valence band densities of states.