X-RAY PHOTOELECTRON SPECTROMETRY
A TOOL FOR CHEMICAL ANALYSIS

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X-ray photoelectron spectrometry

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Many spectrometric techniques have been evolved for the study of materials during the past century. The majority of these, such as visible, ultra-violet and infra-red spectrometry, are concerned with changes in the electronic structure of the outermost electron levels of the atoms involved. The exception to this case is X-ray spectrometry which, although involving core electrons, gives in general very little information on the chemical bonding in the sample.

X-ray photoelectron spectrometry is novel in two ways. Firstly it gives chemical information directly from the electronic core levels, and secondly it can give detailed information about the surface of the sample (i.e. the top few atomic layers) in addition to the bulk material. It is a method which has burst into prominence in the last few years and can be employed to look at electronic levels in atoms and molecules in solids, liquids and gases.

Despite the fact that commercial instruments have been available for only about five years the technique has found applications in chemistry, physics, surface studies, catalysis, biochemistry and mineralogy. Future developments seem destined to increase the range of applications.

PRINCIPLE OF THE METHOD

The principle of X-ray photoelectron spectrometry is simple: X-rays bombard a sample and photoelectrons are ejected from various electron levels in the atoms, according to the expression:

$$E_b = E_x - E_k \dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

where E_b = binding energy of the electron ejected by the photoelectric process,

E_k = kinetic energy of the ejected photo-electron, and

E_x = energy of the bombarding X-rays.

This expression is only approximately correct, for one has to make allowances for certain other factors, including the work function of the electron spectro-meter, charging-up effects, and (rarely) recoil effects.
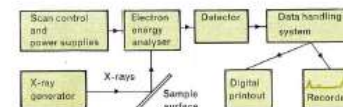
1 *Schematic diagram of the X-ray photoelectron spectrometer*

2 *ES200 photoelectron spectrometer*

3 *Cross-section of ES200*

If X-rays of a known energy are used to bombard the specimen and the energy of the ejected photoelectron is measured, the electron binding energy can be determined. One obvious feature is that the energy of the X-ray must be greater than the binding energy for emission to take place. Further details of the process will be given in a later section of this paper.

A schematic diagram of the apparatus is given in fig. 1. Characteristic X-rays from a known target material irradiate the sample, and the energy of photoelectrons emitted from the surface layer is analysed in the spectrometer. The electron currents reaching the collector can be displayed in either digital or analogue form as a spectrum of current intensity versus electron energy. These data give information about the elemental composition of the sample surface and about the manner in which these elements are chemically combined.

HISTORICAL OUTLINE

Early work was aimed at verifying the photoelectric effect for X-rays, and at a general study of electrons emitted from solids under bombardment by X-rays. This work was carried out between 1910 and 1930 by Louis de Broglie[1] in France and Robinson[2] and his colleagues in England. Both de Broglie and Robinson used magnetic fields and photographic recording to determine the energy of the photoelectrons. The same method, in a more sophisticated form, was used by Kretschmar[3] in 1933 to establish new numerical relationships between the important physical quantities e, e/m and h. After the second world war a great deal of interest was taken in high-resolution β-ray spectrometry: i.e. the determination of the energy of electrons ejected in radioactive decay. Such spectrometry gives information on nuclear structure.

Particularly active were Swedish groups led by Professor Kai Siegbahn who, in about 1955, adapted

an apparatus designed for high-resolution β-ray spectrometry to the study of X-ray photoelectrons. It was soon found that this form of spectrometry (X-ray photoelectron spectrometry) was capable of determining electronic levels in atoms and molecules, and further, of yielding chemical information which had hitherto been unobtainable—the 'chemical shift' whereby the binding energy of an electron is dependent on the manner in which the element is chemically combined.

Despite the excellence of the work by Siegbahn and his colleagues it was some time before the technique was accepted, possibly because much of the original work was concerned with the exploration of the physics of the method. However, after publication of some work on sulphur chemistry plus the appearance of Siegbahn's book[4], which is now regarded almost as the 'bible' of the technique, the method expanded rapidly. Incidentally it was Siegbahn who, about this time, coined the acronym ESCA (from Electron Spectroscopy for Chemical Analysis) which is used in the rest of this paper to denote X-ray photoelectron spectrometry.

AEI Scientific Apparatus Ltd. exhibited the ES100 photoelectron spectrometer for the first time early in 1970, and more than 30 ES100s were installed in laboratories throughout the world by 1972, when the model was superseded by the ultra-high-vacuum version, the ES200.

ES200 ELECTRON SPECTROMETER

The aims borne in mind during the design of the ES200 (fig. 2) were high sensitivity and high resolution, versatility in dealing with electrons over a wide range of energies (up to 4000 eV), easy sample introduction for routine analyses combined with good sample chamber accessibility, and the capability of ultra-high-vacuum operation.

Fig. 3 is a cross-section through the X-ray tube, sample chamber, lens system and hemispherical
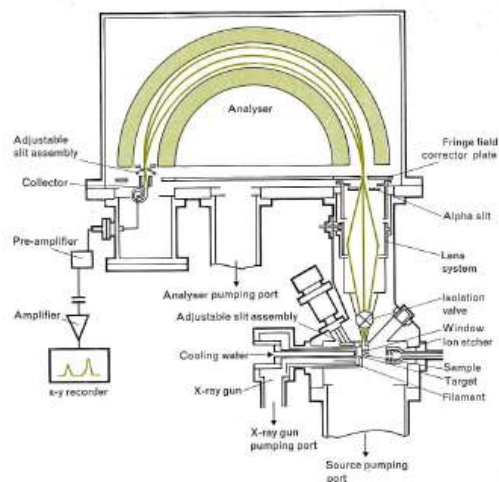
electron-energy analyser; an electrostatic analyser is used because it is easier to shield from stray magnetic fields than is a magnetic analyser. The X-ray gun, sample chamber and analyser are independently pumped, each by a separate system consisting of a liquid-nitrogen cold trap and polyphenyl ether oil diffusion pump backed by a rotary pump. Metal gaskets are used throughout the system so that it can be baked to 250°C for vacuum clean-up purposes.

The X-ray gun is of the 'hidden-filament' type in which the filament is not directly in front of the target. This reduces the rate of contamination of the target by tungsten evaporated from the filament. The gun is isolated from the sample chamber by means of a thin aluminium window through which the X-rays pass from target to sample. The gun filament is earthed and the target operates in the region of $+ 10$ kV to $+ 15$ kV, which ensures that scattered electrons cannot reach the aluminium window with sufficient energy to excite unwanted X-radiation.

The X-ray gun target material is usually magnesium or aluminium, and the Mg Kα or Al Kα line is used to cause ejection of photoelectrons. There are two reasons for this, firstly both magnesium and aluminium have relatively narrow line-widths—0·8 and 0·9 eV full-width half maximum (FWHM), respectively—so a resolution comparable with this can be obtained in the photoelectron spectrum. Secondly the cross-section for photo-ionization of various atomic levels is reasonably high for these radiations so that the technique is sensitive. Obviously atomic levels with binding energies greater than the X-ray energies (1256·6 eV for Mg Kα and 1486·6 eV for Al Kα) cannot be studied. Both types of target can be operated at powers up to 500 W, and both voltage and current supplies are stabilized to 0·1%.

The sample-chamber region is physically well separated from the analyser by the lens system, giving good access

so that six 38 mm diameter ports and four smaller ports can be fitted on the housing to allow a range of sample manipulators and sample preparation and treatment facilities to be attached. The large-diameter diffusion pump and cold trap give the high pumping speed of 100 litres per second at the base of the sample chamber, which, with the baking facilities and auxiliary titanium sublimation pump provided, can give an ultimate pressure in the neighbourhood of 10^{-9} Pa.

The need for ultra-high vacuum (u.h.v.) in the sample region stems from the fact that ESCA is a surface-analysis technique; the escape depth of electrons in the energy range analysed in ESCA is only of the order of 1·5 nm[5]. The rate of surface build-up of a particular contaminant is proportional to the partial pressure of that contaminant near the surface, and with a partial pressure of 10^{-4} Pa a monolayer can be deposited in about one second; hence if sample surfaces are to be kept clean for a period of the order of two hours, pressures of 10^{-8} Pa or lower are required.

Sample-handling facilities include a u.h.v. rotator on which four solid samples can be mounted simultaneously, heated up to 1000°C and analysed in turn. A routine solid-sample shaft can be introduced quickly into the vacuum system by way of a vacuum lock; the shaft supports four samples and covers the temperature range −170°C to 350°C. Solid samples can be ion-etched *in situ* to present a clean surface for analysis or to obtain a profile of the composition throughout the thickness of the sample. In some cases the sample can be evaporated on to the sample holder *in situ* immediately before analysis. An accessory u.h.v. sample-preparation chamber can be fitted when longer-term treatment of samples, or treatments involving corrosive gases, for example, warrant it.

Liquids can be evaporated into the system, condensed on to the cooled sample shaft and analysed in that phase, while vapours can be condensed on to the

sample shaft or studied in gaseous form in a gas cell. The high source-pumping speed, coupled with the low conductance of the electron entrance slit immediately below the electron lens, allows a sufficiently high gas flux to be passed through the source to obtain adequate sensitivity without worsening the analyser vacuum to the point where electrical breakdown occurs.

Electrons ejected from the sample by the X-rays pass through a three-element lens system before they enter the analyser. This is a retarding lens, and in addition to giving greater access around the source by physically moving the sample position away from the edge of the hemispheres it effectively 'improves' the resolution of the analyser system. It does not affect the inherent resolution of the hemispherical analyser, which is ultimately limited by the size of slits used and by machining and alignment tolerances, but does, however, make it more suitable for resolving photoelectron lines. As an illustration, with the smallest slit size used on the ES200, the 125 mm mean radius analyser has a resolving power of $E/\Delta E = 250$, where E is the kinetic energy of an electron in eV and ΔE is the analyser contribution to the line width in eV. Most lines of interest in ESCA lie between 0 and about 1500 eV (remember that Al Kα — 1486·6 eV). At 1300 eV the smallest line width which one could expect, using the analyser alone, is $1300/250 = 5·2$ eV, which is inadequate for the technique.

If a retarding lens is placed before the analyser we can 'adapt' the hemispheres for such energies. Suppose one retards the electrons to a kinetic energy of 65 eV before they enter the hemispheres; the analyser still has the resolving power $E/\Delta E = 250$, and so the ΔE

term at 65 eV becomes 0·26 eV, which contribution is adequate for all but the most stringent ESCA work. More fundamental limits to resolution are of course set by the X-ray line width, and the Heisenberg spread in the binding energy of the electrons in the particular atomic shell which is being examined. It can be shown that the use of a retarding lens in conjunction with an analyser in no way impairs sensitivity.

Two modes of scanning the analyser and lens potentials are available with the ES200. In the first mode the electrons being analysed are retarded to 5% of their initial kinetic energy before they enter the hemispheres. The line-width contribution of the analyser is therefore proportional to energy, so that the resolution of the system improves at the low-kinetic-energy end of the spectrum, but at the expense of sensitivity. A fixed potential difference is applied between the two hemispheres in the second mode so that electrons traverse the analyser with a fixed kinetic energy of 65 eV regardless of their initial kinetic energy. This gives rise to a constant line-width contribution together with enhanced sensitivity at the low-kinetic-energy end of the spectrum. The analyser and lens supplies allow electrons with energies up to 4000 eV to be studied, and the stability of the circuitry is such that the energy scale of the spectra is constant to better than ± 50 mV over many hours.

A Channeltron electron multiplier is fitted in the collector, and is preceded by a four-position slit similar to that used in the source, so that the resolution of the instrument can be varied from outside the vacuum system. The multiplier is operated with a gain of 10^6 to 10^7, and the output pulses are coupled via a charge-
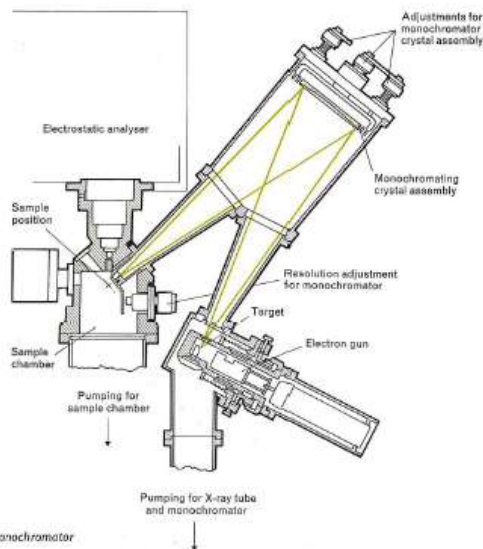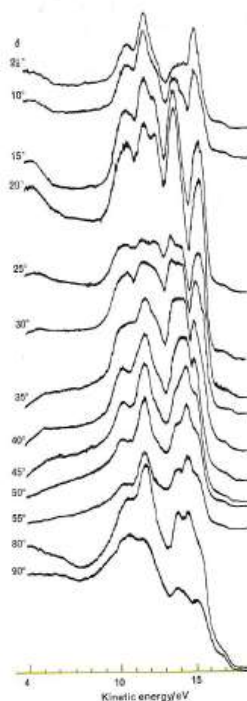

4 Cross section of ES200 sample chamber and monochromator
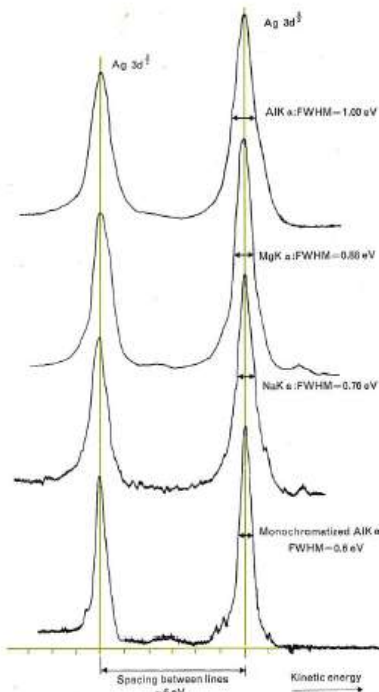
5 Silver spectra using different X-ray radiations

6 MoS₂ ultra-violet spectra

sensitive pre-amplifier to a main amplifier. The signal can be displayed either digitally as the output of the scaler/timer unit on printed or punched paper tape, or in analogue form as the output of the ratemeter plotted on an x-y recorder.

A computer-based data-handling accessory provides additional facilities, such as an elemental programme which allows automatic scanning of selected energy regions in which major peaks from particular elements occur. Repeat scans of a spectrum can be summed in the multi-channel-analyser mode of the system to give statistically improved data. The accessory also provides a deconvolution programme for resolution enhancement.

ES200 ACCESSORIES

One of the most recent attachments for the ES200 system is an X-ray monochromator (Drummond et al[16]) giving Al Kα radiation with a narrow line-width which can be used for high-resolution studies of binding-energy levels up to 1487 eV.

The width of a photoelectron line is dependent on the characteristic radiation used to excite it. Assuming that the appropriate terms can be added in quadrature, the observed line-width is given by the expression:

$$W_{obs}^2 = W_{X-ray}^2 + W_{spect}^2 + W_{C.level}^2, \quad ..2$$

where W_{obs} = observed FWHM width of photo-electron line (eV)

W_{X-ray} = FWHM width of the exciting X-radiation (eV)

W_{spect} = aberration and slit contribution from electron spectrometer (eV)

$W_{C.level}$ = intrinsic FWHM width of the core level being investigated (eV).

Equation 2 neglects spurious broadening effects, such as the build-up of variable electrostatic charge on the sample surface (if the sample is an insulator).

Using Mg Kα radiation we can obtain an overall line-width of 0·88 eV for the 3d levels of silver; this suggests that the intrinsic core level width is of the order of 0·3 eV for these levels. Using the ES200 X-ray monochromator we can obtain an overall line width for silver 3d levels of 0·57 eV, which infers an X-ray line-width for the monochromated Al Kα of 0·3 to 0·4 eV.

A section through the prototype monochromator attached to the ES200 instrument is shown in fig. 4. The X-ray line we have chosen to monochromate is

Al $K\alpha_{1,2}$; normally this has a natural line-width of 0·9 eV, but it is possible by selecting only a part of it, to reduce the width of the exciting radiation to 0·3 eV.

A fine-line source of Al Kα is produced in the X-ray gun, and the appropriate energy and spread of energy (1486·6 eV and 0·3 eV respectively in the case of Al Kα) are diffracted by three quartz crystals mounted on a torroidal former. The crystals are cut parallel to the (10$\bar{1}$0) planes, where the 2d spacing is 0·852 nm and the appropriate Bragg angle for Al Kα is 78·5°. Quartz was chosen because it bends elastically without affecting its high-quality diffracting ability; it has a high 'reflectivity' for Al Kα ($\approx$ 30-40%), and 78·5° is a suitable Bragg angle to work with. Because of the geometry of the system the X-ray flux reaching the specimen is reduced compared with the normal X-ray gun in the ES200 (compared on a watt-for-watt basis of electron-beam power expended in the respective X-ray guns). This loss can be made up, should it be necessary, by means of a multiple collection system at present under development.

An experimental comparison of the effect that various X-radiations have on the width of the 3d photoelectron lines of silver metal is shown in fig. 5. The improvement effected by the monochromator is obvious.

Monochromatic radiation has other advantages besides improving the resolution of ESCA. The first is that the monochromator removes satellites of the $K\alpha_{1,2}$ line, thus peaks due to $K\alpha_{3,4}$, $K\alpha_{5,6}$ and Kβ are eliminated from the ESCA spectrum. The second advantage is that Bremsstrahlung (continuous or white X-radiation) is eliminated from the X-ray beam. This has the effect of significantly improving the signal-to-background

ratio of the photoelectron peaks, which means an increase in the limits of detection of the technique.

In addition ultra-violet irradiation of gases and solids has been carried out on the ES200. U.V. photoelectron spectrometry, in particular that using HeI and HeII resonance lines on gases, is a well-established field (Turner et al[17]) and we shall not discuss it further here other than to say that the attachment for the ES200 gives as good a resolution as any other instrument. The u.v. photoelectron spectrometry of solids is not a new field, but it is one in which some consistency is now being established because of the reliable ultra-high-vacuum ($< 10^{-8}$ Pa) conditions now attainable. Although one can explore only the valence electron systems with the HeI and HeII lines (energy = 21 and 41 eV respectively) it has proved very useful for studying chemisorbed species on the surfaces of metals and for indicating the structure of the valence band of solids. An advantage over X-rays is the much better instrument resolution using u.v.—it is only a few meV. Spectral peaks of this width are rarely realized on solids because of solid-state broadening effects, but they are realized in gases.

As an example of the improved resolution resulting from using u.v. on solids, a series of HeI spectra from the work of Williams et al[18] is given in fig. 6, which shows the angular variation of intensity of photoelectric emission from molybdenum disulphide. This angular variation has been interpreted by these authors in terms of the geometry and filling of the molecular orbitals of MoS_2.

It will be shown in the following section how Auger electrons can arise from X-ray bombardment of the sample; such electrons can also be emitted when the
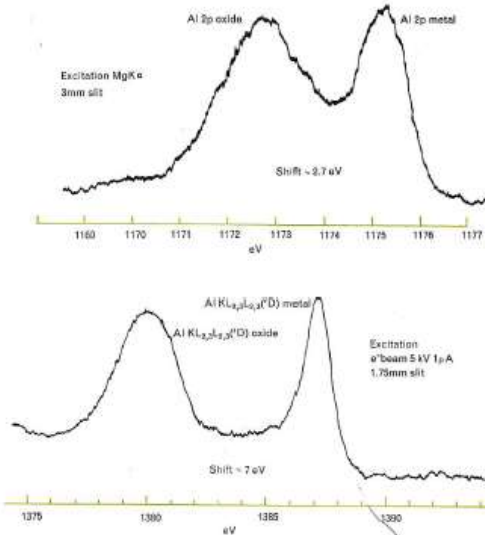
sample is bombarded with electrons of a few keV, and this technique is known as A.E.S. (Auger Electron Spectrometry).

Using an ES200 system and a 5 keV electron gun attachment, good Auger peaks have been obtained with a relatively narrow width and have demonstrated a chemical shift for light elements. The high resolution of the ES200 analyser allows true peak profiles to be obtained. An example is shown in fig. 7, where the metal/metal-oxide shift is shown for aluminium when the same sample is studied by ESCA and by electron-induced A.E.S. It will be seen that the shift in the Auger case is greater than in the ESCA case. This is not unusual at low atomic numbers.

ESCA SPECTRA CHARACTERISTICS

Before going on to discuss some of the many applications of the ESCA technique the features of photoelectron spectra obtained from such an instrument as the ES200 will be discussed.

ESCA spectra have certain characteristic features as a result of shell vacancies caused by X-ray bombardment and other physical processes. In order to explain the spectrum we shall briefly discuss these physical processes. Fig. 8 schematically illustrates the processes of vacancy creation and de-excitation. In fig. 8a an

8 Shell vacancy creation and de-excitation methods

incoming X-ray quantum creates a K-shell vacancy* in an atom by ejecting an electron from the K shell with kinetic energy given by $E_k = E_{X-ray} - E_{bk}$ (cf. equation 1), where E_{bk} = binding energy of the electron to the K shell, E_{X-ray} = energy of the bombarding X-ray quantum.

For the moment we shall leave the photoelectron moving out of the sample while we consider how the K-shell vacancy is filled. It can be filled in one of two ways: fig. 8b illustrates the fluorescent effect—in this case an electron from an outer shell falls into the K shell with the simultaneous emission of the corresponding amount of energy as X-radiation (L_3-K gives rise to $K\alpha_1$ X-ray of energy $E_{K}-E_{L3}$ eV). The creation of this fluorescent X-ray forms the basis of the well-established analytical technique X-ray fluorescence (XRF). Fig. 8c shows an alternative way in which the vacancy can be filled by the Auger effect[9]. If an L-shell electron is simultaneously emitted then the emitted electron is an Auger electron designated KLL type.

The energy of an Auger electron is given by the expression (Yasko and Whitmeyer[10]):

$$E_R - E_S - E_{S}' - E_{R_1} \quad \dots\dots\dots\dots\dots\dots\dots 3$$

where E_R = kinetic energy of electron emitted from R shell of atom,

E_S = electron binding energy of S shell of atom, the shell in which the vacancy has occurred,
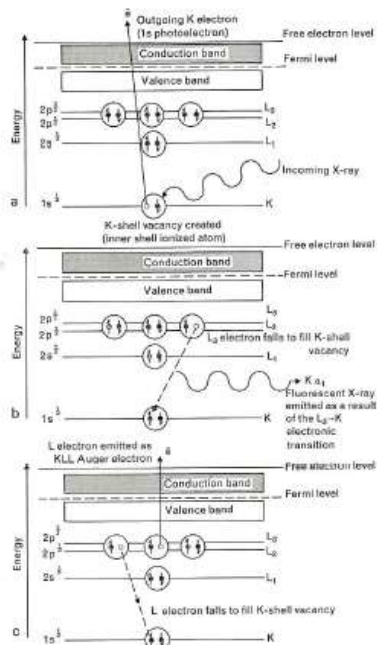
E_{S}' = electron binding energy of S′ shell of atom,

E_{R_1} = binding energy of R shell of atom already singly ionized where atomic no. = Z ($E_R \approx$ electron binding energy of R shell of atom of atomic no. Z + 1).

The Auger and X-ray fluorescence effects are competing methods of de-excitation. It is found that for high-energy excitations (> 1000 eV) the fluorescent effect predominates, while for low-energy excitations the Auger process predominates. Incidentally it will be noted that the energy of the Auger electron is independent of the X-radiation used (cf. equation 3).

As stated previously we expect to see, in an ESCA spectrum, peaks due to photo and Auger electrons. However, one must realize that the escaping electrons will lose energy as they leave the sample owing to collisions of various types, and this results in a rising background on the low-kinetic-energy side of the peak. Fortunately for the method the energy losses are quantized, and there is a discrete gap between the rising background and the electron peak in question.

Fig. 9 illustrates the features that have been described in the previous paragraphs. It is the ESCA spectrum of polytetrafluoroethylene (PTFE), recorded when the sample is irradiated with Mg Kα X-radiation. The following characteristic features will be noted: photoelectron peaks due to carbon marked C_{1s} and C_{2s}, and due to fluorine marked F_{1s}, F_{2s}, F_{2p}; a series of KLL Auger peaks of fluorine; the region of energy loss electrons on the low-kinetic-energy side of the peaks.

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*The X-ray quantum need not confine itself to a K shell; it can cause vacancies in any electronic level provided it has sufficient energy. A K shell is taken only as an example in the present case.

7 Comparison of a photoelectron spectrum with an electron-induced Auger spectrum

9 PTFE spectrum
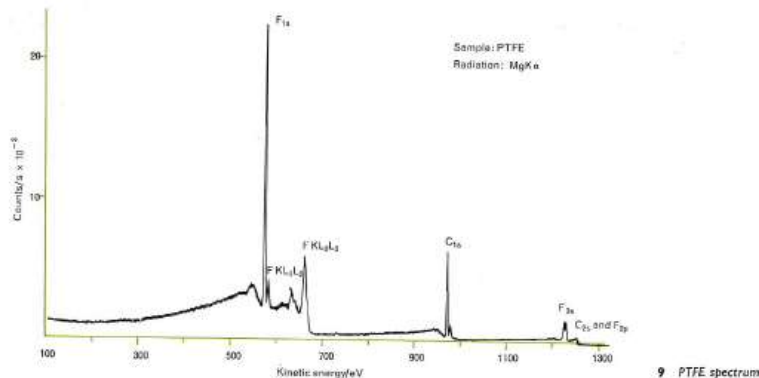
If one knows the binding energies of various electronic levels in different atoms then one can identify elements present in a sample. Tables of binding energies exist (Siegbahn *et al*[4]) and rapid qualitative analysis is possible. However, the feature which gives ESCA its teeth, so to speak, is the existence of the chemical shift in the X-ray photoelectron spectrum. This arises because the binding energy of the core electrons can be altered by a variation in the valence electron system. These outer electrons affect the attraction that the nucleus exerts on the core or inner shell electrons. If the number of valence electrons is reduced then the attraction of the inner shells to the nucleus is increased and so the binding energy of these shells is increased.

As the valence-shell arrangement depends on the chemical state of the atom involved, then the energy of the core electrons will depend on the chemical state.

Fig. 10 shows perhaps the most famous X-ray photo-electron spectrum to date. It has been shown many times before and it does illustrate the features of the chemical shift in a most dramatic way. The sample is the ester ethyl trifluoroacetate $(CF_3COOC_2H_5)$ and the spectrum shows the carbon 1s region as excited by Al $K\alpha$. The ethyl trifluoroacetate molecule contains four carbon atoms, and each atom is in a different chemical environment. One is bonded to three fluorine atoms; fluorine is very electronegative and tends to draw away valence electrons from the carbon, re-sulting in the core levels becoming much more tightly bound than in an isolated carbon atom (the shift is about 8 eV). The other carbon atoms are in different environments and so have different values for the binding energy as shown in the figure.

So far chemical shifts have been reported for 84 elements, according to Schwartz[11]. It is because of the chemical shift that ESCA finds application in so many fields (cf. nuclear magnetic resonance which has a more sensitive chemical shift effect than ESCA but which is applicable only to elements with suitable isotopes).

Before discussing a few ESCA applications it is perhaps worth mentioning, albeit only briefly, some of the more unusual ways ESCA spectra can be modified in certain conditions. Line (level) splitting can occur in para-magnetic molecules (e.g. FeF_3) owing to interaction of some of the core levels with unpaired electrons in the valence band. Splitting due to electrostatic gradients within the atom has also been claimed. In addition there may be configuration interaction peaks, plasmon loss peaks and certain other peaks. These effects can yield useful chemical information about the specimen under investigation. For details of such effects the reader is referred to the proceedings of an International Conference on Electron Spectroscopy held in Cali-fornia in 1971 (Shirley[12]). In addition to the effects so far mentioned in this paragraph there are artefacts of the X-radiation which are generally caused by satellites of the main peak of the exciting X-radiation. Thus in the spectrum of PTFE in fig. 9, the Mg $K\alpha_{1,2}$ is accom-panied by the X-ray satellites designated $K\alpha_{3,4}$, $K\alpha_{5,6}$, and $K\beta$. These satellites give rise to additional peaks on the high-energy side of photoelectron peaks, although their position is well known so that their contribution to

10 Ethyltrifluoroacetate spectrum
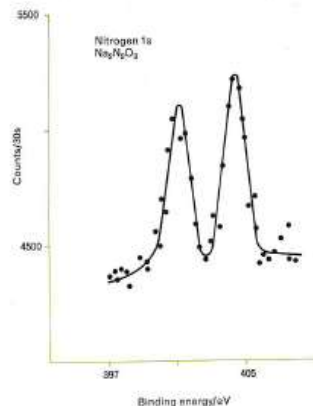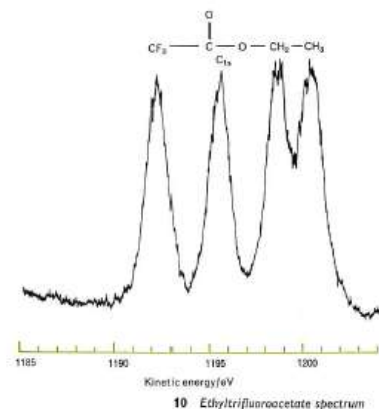
particular spectral regions can be calculated and com-pensated for. They can alternatively be eliminated by the use of an X-ray monochromator.

TYPICAL APPLICATIONS OF ESCA

ESCA can be used to evaluate numerous problems, and the four discussed briefly in the next few paragraphs are chosen to show its versatility. The four applications are in the fields of chemical structure determination, determination of the type or degree of chemical bonding, problems in surface chemistry and problems connected with wear and corrosion.

Chemical Structure Determination

The chemical shift can be an aid in determining chemi-cal structure. Early work by Swedish groups established the structure of various sulphur-containing com-pounds, such as those products arising from the action of hydrogen sulphide on (a) 2-4-pentanedione, and (b) α—angelica lactone (see Schwartz[11]).

The example chosen of the determination of a chemical structure was carried out in the relatively early days of ESCA and is described by Hollander and Jolly[13] who, with Hendrickson, determined the structure of the anion of Angeli's salt (the oxyhyponitrite ion). The possible structures for the anion are:

(1) $O - N - O - N^- - O^-$

(2) $O = N - N \big\langle\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$

(3) $^-O - N = N - O - O^-$

The nitrogen 1s spectrum of the anion is shown in fig. 11; it is a doublet, indicating the presence of two forms of nitrogen bonding. The symmetrical structure (1) is thus eliminated. The separation of the lines is some 4 eV, and molecular orbital calculations showed that structure (2) was compatible with the X-ray photoelectron spectrum of the ion.

Determination of Type of Chemical Bonding

As an example of how ESCA can aid such investigations we shall briefly consider the work of Barber *et al*[14,15]

11 Oxyhyponitrite ion spectrum

COMPARISON OF BINDING ENERGIES IN SOME TRANSITION METAL CARBONYLS

	Binding energies relative to internal standards*		Binding energies relative to CO	
	1s (C)	1s (O)	1s (C)	1s (O)
Ni $(CO)_4$	3·4 eV	1·0 eV	−2·2 eV	−1·4 eV
Fe $(CO)_5$	3·2 eV	0·8 eV	−2·4 eV	−1·6 eV
Cr $(CO)_6$	3·1 eV	0·7 eV	−2·5 eV	−1·7 eV
W $(CO)_6$	3·1 eV	1·0 eV	−2·5 eV	−1·4 eV

* Carbon 1s in hexane; Oxygen 1s in water

on the transitional metal carbonyls (e.g. Ni$(CO)_4$, Fe$(CO)_5$, Cr$(CO)_6$). The CO groups are attached to the metal atom via the carbon atom and the M-C and C-O bonds are co-linear. It is proposed that the carbon monoxide donates electrons to the metal and that some $d_\pi - p_\pi$ bonding adds some strength to the bond. This would, following the explanation of Cartmell and Fowles[16], give rise to the tentative formulation $Ni^{4-} - (CO)_4^+$ for nickel carbonyl and indicates a build-up of negative charge on the metal atom.

Some of the negative charge can be neutralized by back donation of electron charge from the doubly filled d orbitals of the metal atom to the vacant π orbital on the carbon atom—the amount of back donation is uncertain and ESCA can help in this matter. Barber *et al* measured (with an ES100) the binding energies of the carbon and oxygen 1s levels in the carbonyls. The results are shown in the table.

In the four carbonyls listed the C 1s and O 1s electrons are less tightly bound than in free carbon monoxide (≈ 2.5 eV for C 1s and ≈ 1.5 eV for O 1s). Barber *et al* suggest that this represents an increase in electron density on the ligands of the carbonyls as compared with free CO. These experimental results would suggest that there is more π back bonding into the virtual orbital of CO (2π) having a large 2p component, than σ donation from the highest filled 'lone pair' orbital of CO (5σ). The amount of back bonding in the Barber model is larger than previous results suggested. The bonding in these compounds has been studied many times, both theoretically and experi-

12 CO on tungsten
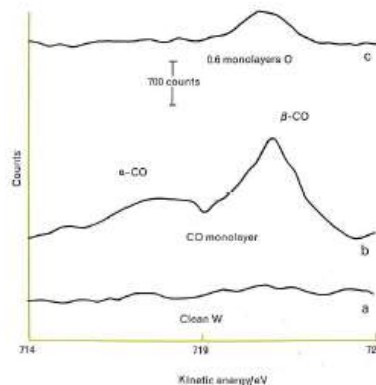
mentally, by rather indirect methods in the past, but now the advent of ESCA has given a definite solution.

Surface Studies and Surface Chemistry

The depth from which a 1000 eV electron can escape from a solid without energy loss is typically 1·5 nm. Thus ESCA can be applied to many surface studies, as most of the photoelectrons are obtained from the first few monolayers. The example given here is the study of chemisorption of carbon monoxide on polycrystalline tungsten.

The work in question was performed at the National Bureau of Standards (USA) by Madey, Yates and Erickson[17] and it was carried out on an AEI ES200 instrument. These authors showed it was possible to predict the photoelectron yield of one monolayer of carbon monoxide on a tungsten substrate. The calculated yields agree well with the experimentally observed values. Thus one result of the work shows that one can determine the degree of coverage of a surface in a quantitative manner.

In addition these authors have demonstrated the two bonding states for the carbon monoxide on the surface. The O ls signal from the CO on the surface of the tungsten is shown in fig. 12. It is a doublet with peaks at 720·9 and 717·5 eV kinetic energy. The two peaks are interpreted as being due to strongly held β CO states and weakly bound α CO states. The more weakly bound states could be removed by heating to less than 600°C under vacuum; the β peak remained unchanged. Flash desorption measurements indicate that α CO comprises 20% of the monolayer at saturation. The energy difference between the two O ls peaks ($\approx$ 3·4 eV) represents the different chemical bonding between the CO and the metal surface.

Other studies have shown that α CO is bonded through sp hybridized carbon to the surface while the β form has C and O in contact with the metal surface. Thus by an elegantly simple method Madey *et al* have shown that with ESCA one can obtain not only chemical information about adsorbed species but also quantitative data on the degree of coverage of the surface down to fractions of a monolayer.

Wear and Corrosion

The application of ESCA in the study of wear which we consider here is an example in tribochemistry. The work was carried out by Atkinson and Swift[18] and concerns the failure of molybdenum disulphide films under sliding conditions, due to tribo-oxidation.

Well-characterized MoS_2 (particle size 0·7 μm) was run in a 'flat-on-flat' geometry wear-testing rig until failure occurred. The ESCA spectrum of the MoS_2 was examined before and after the run, and some of the results are shown in fig. 13. Fig. 13a shows the Mo $3d^{3/2}$, $3d^{5/2}$ spin doublet and the unresolved sulphur 2p spin doublet of the MoS_2 before treatment. These positions of the peaks correspond to the chemical state of the molybdenum (Mo^{IV}) and sulphur (S^{II}) atoms in the MoS_2. Features of the ESCA spectrum of the failed MoS_2 film are shown in fig. 13b. The Mo spectrum shows a third peak 3 eV lower in kinetic energy than the Mo^{IV} $3d^{3/2}$ peak. This corresponds to a Mo $3d^{3/2}$ level of Mo in a more oxidized state, Mo^{VI}. It corresponds in fact with molybdenum trioxide, which is known to be a product of the tribo-oxidation of MoS_2. In addition the spectrum shows
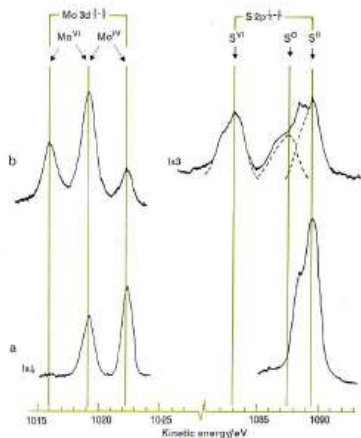
13 MoS_2 spectra from Mg Kα radiation

evidence of some remaining MoS_2. The $3d^{3/2}$ level from Mo in MoS_2 and the $3d^{5/2}$ level from Mo in the more oxidized state coincide in the central peak.

The sulphur 2p level in the failed sample is identified as sulphur in three different states: S^{II} from the original MoS_2, elemental sulphur S^0 and sulphur in a more oxidized state, probably sulphate (S^{VI}). The authors therefore propose that the failure of MoS_2 in the example given occurs as a result of the oxidation of MoS_2 producing compounds with a high friction.

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