

A wizard source of expertise in XPS

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X-ray photoelectron spectroscopy has been in use for the study of materials for 30 years and with considerable success. In retrospect, however, it is clear that the many insights arising from work undertaken in the initial decade (the 1970s) are not well known to new users of the technique. Many of the simpler aids to interpretation, e.g. the use of shake-up satellites, have stood the test of time and of more recent theoretical explanation and could easily be made available through help routines incorporated into the data system. Examples are given of the manner in which the help could be accessed by way of a screen 'wizard', which might also provide a stepping stone to the development of a full expert system. Copyright © 2002 John Wiley & Sons, Ltd.

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INTRODUCTION

The past 30 years has seen the introduction and development of XPS from a new technique to maturity and none has made a greater contribution to its reliable use as an analytical technique than Martin Seah. Many of the advances made under his leadership have now become embedded in the technique, e.g. in the use of a standard transmission function for spectrometers and in the use of calibration procedures for quality control. Such facilities are available to novice and expert alike. Other knowledge built up during the period is, however, much more likely to be accessed and used effectively by the expert than by the novice. This is an important omission and the purpose of this brief contribution to the special issue recognizing Seah's achievement is to highlight four instances in which a database assistant or 'wizard' could be used to make more anecdotal yet reliable information available to novices (and forgetful experts). The areas chosen for examples are: the use of satellites to corroborate in the identification of chemical state; the use of photoexcited Auger spectra and the chemical state diagram; access to bremsstrahlung-excited Auger lines; and trial estimation of layer sequences in the near-surface region. In each of these areas there is information that, although of secondary level, is completely reliable and should be made available to the novice user in some convenient manner through the medium of the data system. The inclusion of type of help in the form of a 'wizard' in a typical data system would perhaps even pave the way to the full implementation of an expert system.

SHAKE-UP SATELLITES

Satellites are a good example of the secondary information that is available in the XPS spectrum and have been used to recognize certain chemical states in the context of corrosion for over the whole 30-year period. Those most widely known are associated with divalent ions of copper and nickel (Fig. 1). Possibly the first recorded use¹ of satellites stemmed from work on the corrosion of cupronickel alloys in steam containing trace quantities of oxygen.² The oxidation of nickel at room temperature and at 500 °C was compared with that of cupronickel at 50:50 and 70:30 compositions. The use of satellites illustrated that at room temperature the surface oxide was 100% NiO and that the situation reversed in favour of CuO at high temperature. It was pointed out that satellites might be used in quantification and the relative heights of the satellites were compared with those of the pure oxides and used to infer that metal or lower valence state species were not present in the spectrum. This early example is given emphasis because it indicates the degree of expertise that was available 30 years ago and yet is still not automatically presented to the user in today's data systems. When copper or nickel regions are called for in analysis, or are found to be present in a survey scan, a wizard could be programmed with the advice shown in Box 1.

The satellites on nickel have proved very useful in identifying chemical states in corrosion studies: nickel in stainless steel was quickly eliminated as a constituent of the oxide film by the lack of the satellite on the 2p peaks of this element.³ However, the presence of satellites is often less obvious than that shown by Cu(II) but still can be important in the identification of iron compounds, for example, as illustrated by a set of standards by Brundle in 1975⁴ and used in a study of the oxidation of iron,⁵ and in the identification of chromium (III) compounds, distinguishing this state from Cr(VI)⁶ as first shown by Allen.⁷ Examples of these satellites are given in Fig. 1. Current work is concerned

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with identifying the origin of these and other satellites, which are known to have several possible origins, and recent

work by Moler *et al.*⁸ at the Advanced Light Source is a good example of this, showing that even in the case of Ni metal the small satellites result from both single electron and multi-electron transfers into the unfilled d-band. Their work using photoelectron diffraction shows that the single electron transfer occurs as a single event in phase with ionization of the core electron.

PHOTOEXCITED AUGER SPECTRA

Another important area for investigation in the 1970s concerned photoexcited Auger spectra, often now referred to as X-ray-induced Auger electron spectroscopy (XAES). Once again, interest was driven by a need arising from the oxidation of copper. The chemical shift between copper and the Cu(I) state is negligible but the final state effects resulting from polarization of the surrounding ligands are doubled on the Auger peak and this gives rise to a significant shift⁹ (Fig. 2). Wagner showed, simply, that the differing shifts on Auger and photopeaks were best summarized by way of a parameter, the Auger parameter, that enabled the recognition

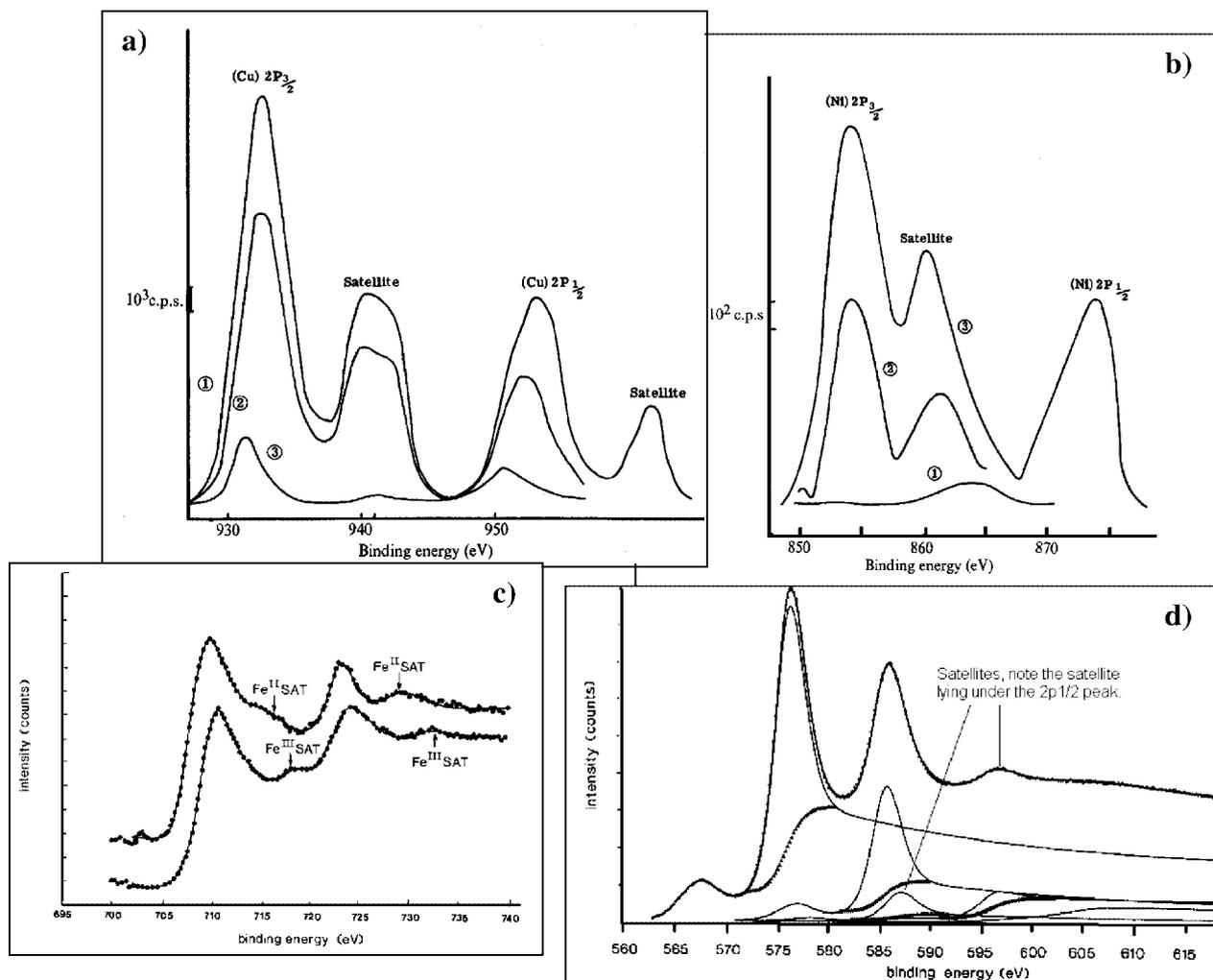


Figure 1. Satellites on the transition metals. (a,b) The importance of satellite peaks was recognized in 1971. In this example using the satellites on Cu and Ni it is shown that the native oxide on 70%Cu–30%Ni alloy (curve 3) is NiO, but that after oxidation at 500 °C (curve 1) it is CuO. The 50%Cu–50%Ni alloy is a mixture of both oxides after oxidation (curve 2).¹ (c) The importance of the satellites on Fe oxides was recognized in 1975;⁴ here, they were used to distinguish the oxides in a study of the oxidation of iron chromium alloy.⁵ (d) The satellites on chromium(III) oxides⁶ were described in 1976⁷ and can be used to distinguish the (III) and (IV) states.

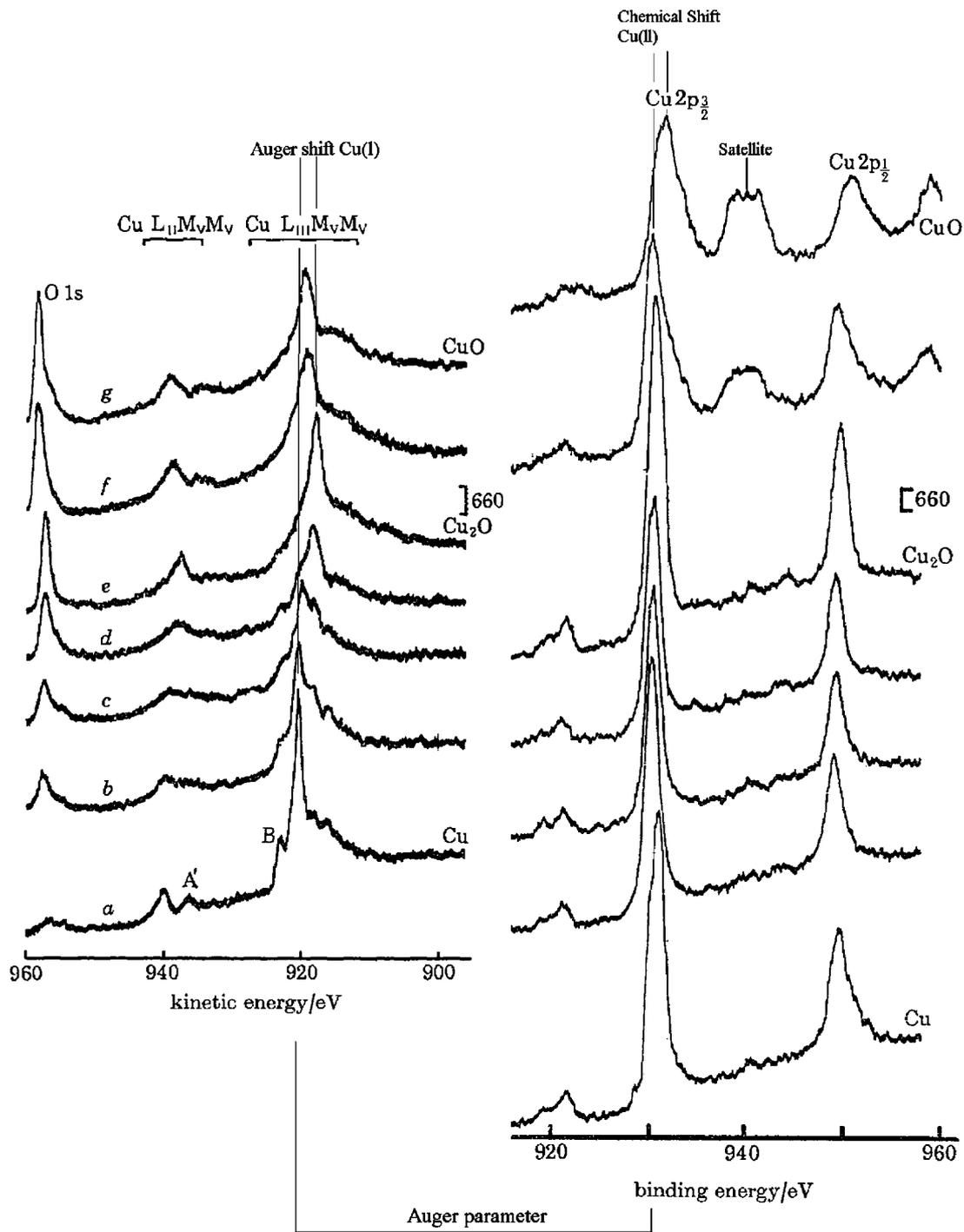


Figure 2. The oxidation of copper taken from a 1974 publication,⁹ with annotations added to show the sources of chemical state information and marked to show the derivation of the Auger parameter.

of many chemical states.¹⁰ Interpretation of the Auger parameter shows that in conductors the shift is largely determined by intra-atomic relaxation and is a rather small effect;¹¹ in insulators, the shift is largely due to extra-atomic relaxation and is much larger. Wagner built the principle of the Auger parameter into the Chemical State Diagram,¹² which is used to the present day as an empirical means of identification and is especially useful in the presence of charging.

Unambiguous identification of chemical state is the first reason for using the chemical state diagram but an important second reason is that there is no necessity to correct

spectra for electrostatic charging of non-conductors. When the Auger and photopeaks are recorded at the same time, all charging influences appear as orthogonal movements on a line representing a given Auger parameter. This can be of interest, for example, it is noticeable that metals appear on the far right of the diagram (for examples see Ref. 13) and insulating oxides appear on the left of the diagram. However, the present-day view, expressed by Moretti,¹⁴ is that the price paid for ignoring charging is that initial and final state effects are confused. By plotting charge-corrected data, Moretti points out that the data for compounds sharing

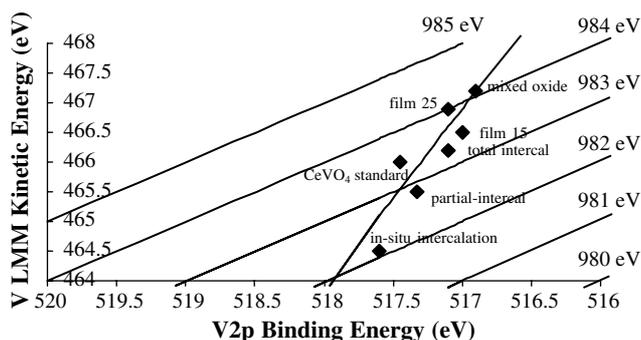


Figure 3. A recent example of a chemical state diagram (CeVO_4) has been deposited in various thin films and intercalated with Li ions to differing levels. The 1 : 3 line represents the initial state and it is clear that this is similar for all preparations; the 1 : 1 line represents the final relaxed state and it is clear that this changes with the degree and type of intercalation.

Box 2

These elements have well-defined Auger peaks: shall I include an Auger peak in the set of scans, calculate the Auger parameter and relate this to possible compounds using the Chemical State Diagram?



the same initial state, i.e. sharing a similar local potential as determined by the Madelung potential and related chemical state effects, align on a common line running across the Chemical State Diagram.¹⁵ A recent example used to analyse the effect of intercalation of Li in thin films of CeVO_4 is given in Fig. 3. In this diagram for vanadium, the various thin films and intercalated samples lie on a common initial state line, showing that the processing routes had not affected their crystallographic structure. The different examples, however, differ significantly in Auger parameter showing that the electronic polarizability of the structure is influenced by intercalation.¹⁶ For many elements the advantage of recording Auger spectra together with photoelectron peaks is enormous. It is an advantage that is often missed and again a helpful wizard might offer advice as exemplified in Box 2.

HIGH-ENERGY X-RAY SOURCES AND BREMMSTRAHLUNG EXCITATION

In the course of trying to analyse aluminium in the presence of copper, as in aluminium brass and the aluminium

bronzes,¹⁷ it was found that the overlap between Al 2p and 2s and Cu 3p and 3s, respectively, is fatal, made worse by the fact that Al is often oxidized and the chemical shift then makes the overlap almost exact. In the course of work using higher energy sources,¹⁸ able to excite Al 1s (Fig. 4), and so rectify the situation, it became apparent that Auger peaks of aluminium and silicon created by the bremsstrahlung¹⁹ in non-monochromated Mg and Al $K\alpha$ radiation were perfectly able to provide the needed analysis (Fig. 5). Aluminium and silicon both have large shifts in Auger parameter, and the bremsstrahlung peaks were equally reliable and useful for the determination of Auger parameters. These and other useful Auger peaks are often found in the 'negative binding energy' region of the spectra and are not, therefore, recorded without some degree of forethought. A wizard (Box 3) could easily ensure that this opportunity is not missed.

ESTIMATION OF LAYER THICKNESS

By 1975 Sherwood²⁰ and others had introduced the idea of measuring the thickness of a native oxide by a simple intensity ratio, using the fact that for a native oxide the effective depth of analysis can be assumed to be the same for oxide and metal. More generally, in corrosion and

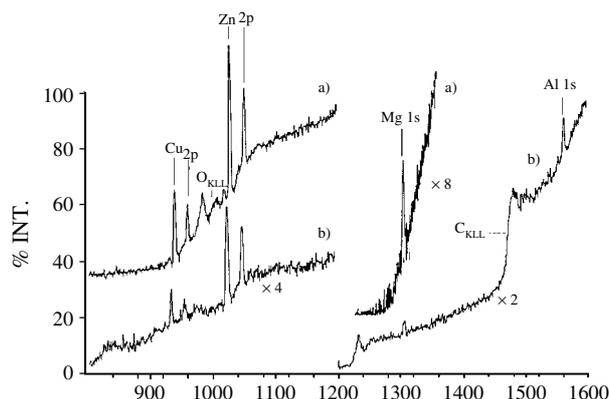


Figure 4. Example of the use of a higher energy x-ray source to reveal aluminium in films on aluminium brass: (upper spectrum) Al $K\alpha$; (lower spectrum) Si $K\alpha$. Aluminium is masked by copper peaks in Mg and Al $K\alpha$ radiations.¹⁷

Box 3

There is a clash between the elements in this analysis: shall I include Auger peaks that lie outside the normal range of binding energy?



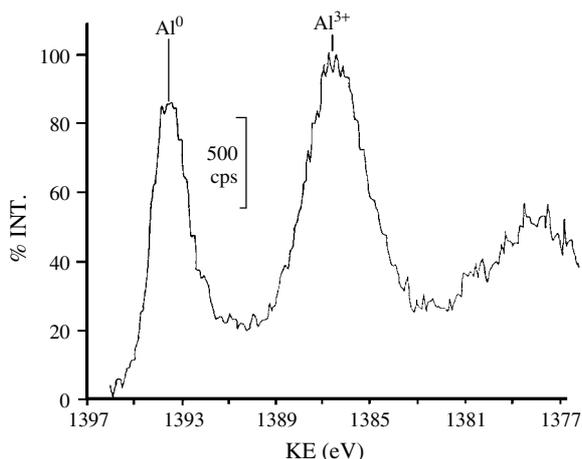


Figure 5. Example of chemical state information for Al that is available in the bremsstrahlung-excited KLL Auger peak. This peak appears in the negative binding energy part of the spectrum when Mg $K\alpha$ is the exciting radiation.¹⁹

electrochemistry, we are dealing with a minimum of two layers—contamination plus the oxide film—and thus a more detailed ‘stratification analysis’ is required. In the case of passivating layers, these may be of similar thickness and hence amenable to study by the change in peak intensity when the sample orientation is changed between a low and a high angle of take-off.³ It was shown much more recently that there is an advantage, for stratification, in ratioing the whole survey spectrum obtained at two angles.²¹ Another form of thickness measurement stemmed from work undertaken in order to determine whether a surface was active as a cathode, for which it was necessary to measure the deposit thickness of $Mg(OH)_2$ on copper.²² The mean free paths are now different and so it was necessary to plot a calibration curve. In the last year all these various measurements have been combined by Cumpson²³ to give a simple nomogram that he refers to as a ‘thickogram’. There has been much published work on ‘non-destructive depth profiling’ making use of angle-resolved XPS data but the detailed analysis by Seah and Cumpson has shown that a cost-effective stratification can be obtained with two angles.²¹ Modern instruments use a lens design to provide data resolved into at least two angles, and older instruments can provide much the same data by the use of two radiation sources.²³ Thus, this stratification method applied to the survey scan can give useful information, as indicated by the wizard in Box 4. Whereas in the earlier examples the wizard would be prompted by the setting up of the spectra to be included in the experiment, the wizard here would be prompted by the request for a second angle.

Finally, in an illustration of possible routes to an expert system²⁵ it was suggested that the thickness of contamination could be estimated directly from the atomic concentration of carbon in the analysis, using the survey scan if this can be quantified automatically. Knowledge of an approximate overlayer thickness then permits an automatic correction of the intensities for scattering losses in the contamination layer.²⁶ Again, a wizard should be able to offer this facility (Box 5). This wizard would appear at the time of

Box 4
Survey scans obtained at different angles permit a trial stratification of the surface structure: shall I implement this feature?



Box 5
Your carbon 1s signal indicates a contamination layer of x nm: shall I use this value to correct the quantification?



quantification of the spectrum, i.e. after the experiment was complete.

ENERGY LOSS STRUCTURE AND BACKGROUND

Interest in the background structure is another topic that spans the 30 years of XPS commercialization. In 1971¹ it was already possible to include the phrase: ‘the background rises steeply as is typical of samples that have not been prepared by evaporation or by ion stripping within the spectrometer itself’. Qualitatively, the slope of the background after peaks gives another good guide to surface stratification and has been of much value in corrosion studies, for example, in showing the manner in which manganese, chromium and iron interact within an oxide film during vacuum heat treatment:²⁷ the procedure has been placed on a fully quantitative basis by Tougaard²⁸ and a wizard might well give a reminder of his informative web site²⁹ (Box 6). To be most useful, and not merely annoying, this prompt would entail automatic measurement of the slope following peaks. It could be prompted, for example, by a finding that the slopes following metallic peaks were different, implying segregation in depth as shown in Fig. 6.⁵ The region after the peak is dominated by extrinsic effects (i.e. losses experienced by the photoelectron during transport to the exposed surface)

Box 6

The post-peak slope of the background of the metallic peaks suggests a non-homogeneous depth structure: have you considered using QASES²⁶ to interpret this?



but the region close to and including the peak is dominated by intrinsic losses (i.e. losses associated with the concomitant

excitation of an outer electron during photoionization of the core). It is these losses that give rise to the Doniach–Sunjic shape, described by the eponymous authors in 1970.³⁰ The intrinsic losses decrease in a manner that is often symmetrical with and complementary to the extrinsic losses, so that an approximately horizontal tail is often found on relatively clean samples.

Doniach and Sunjic gave an analytical shape for the skewness resulting from intrinsic losses and Tougaard has given an analytical shape for the extrinsic background; added together, the shape of the XPS peak and background is well represented. However, neither of these give an easily closed window over which to integrate for quantification. This central problem in quantitative analysis is still overcome using the approach suggested by Shirley in 1972.³¹ The Shirley background subtracts both components, intrinsic and extrinsic, leaving an approximately symmetrical peak that is ideal for quantification. This simplification inevitably means that any information contained within the background is

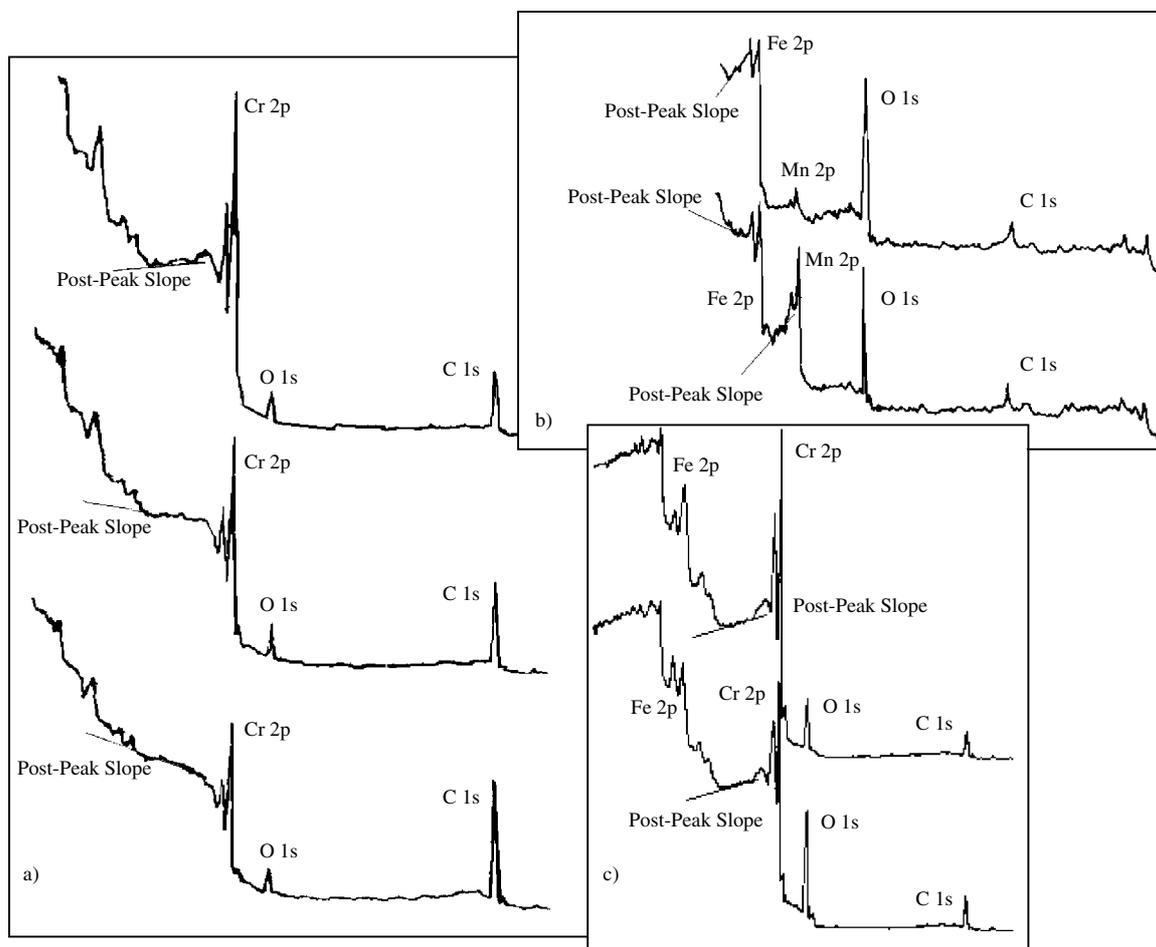


Figure 6. The post-peak slope (p-ps) and near-surface structure. (a) In this set of spectra, carbon is deposited onto chromium, giving rise to a steady increase in the negative value of the energy-loss tail (p-ps) of the Cr 2p peak as the overlayer increases in thickness. (b) Here, a carbon steel has been annealed in a vacuum, leading to the replacement of iron oxide by manganese oxide. Note that the positive p-ps of the Fe 2p peak becomes negative whereas the Mn 2p peak gains a positive slope, indicating that this oxide now forms the surface layer. (c) In these spectra the chromium in stainless steel has been oxidized selectively. Because chromium oxide remains the surface phase, there is no change in the Cr 2p peak p-ps. However, inspection of the Fe 2p peaks shows that the local background at this peak becomes negative in value, indicating that the chromium oxide has increased in thickness (examples are taken from Ref. 27 and re-annotated).

lost. Tougaard has concentrated on the recovery and use of the extrinsic background as an aid to stratification analysis, whereas in collaboration with Salvi the author's attention has been focused on the magnitude of the intrinsic losses.^{32–35}

Doniach and Sunjic considered their line shape to be that appropriate to metals but similar line shapes are found for many oxides of the transition metals and for adsorbed species on metallic substrates. In the work of Castle and Salvi the line shape has been defined by the height of the tail (if horizontal, or its projection if not) measured at the position of the peak maximum. This parameter has the name 'shape parameter' and acts as the integration constant, which defines the magnitude of the Shirley background and hence the overall shape of the peak. The shape parameter is intrinsic to the orbital of a given element and changes in a regular manner along the rows of the Periodic Table. For third-row elements a maximum is reached at iron.³⁵ Curve fitting that ascribes different extrinsic backgrounds (i.e. sloping tails) to each component as well as predefining the height of the intrinsic step for each peak, is able to give data on both composition and depth of emission.³⁴ Others have taken similar routes to data analysis in the context of corrosion studies and a good theoretical analysis in the context has been provided by Graat *et al.*³⁶

The shape parameter, κ , has been used in a variety of studies of bonding in aluminides³⁷ and silicides³⁸ and it has been shown, also, that it should be a good indicator of chemisorbed states.³⁹ In aluminides it correlates well with the Auger parameter and has given information on the importance of p–d hybridization to the bonding states. Eventually, a wizard might be the best means of giving assistance in the choice of 'Shirley' background parameters drawn from those now being assembled.

CONCLUSION

This review has tried to focus on topics, driven by the needs arising from corrosion science, that have been the subject of continual development through the 30 years of XPS availability. It has been shown that many of these are capable of giving very reliable information relevant to a number of technologies. Incorporation of simple knowledge-based assistants into data systems would be a sensible way of making this information available to those who are not expert in the field of XPS. Wizards can do only so much; they are likely to be ideal for rather unequivocal and simple pieces of advice, and examples have been drawn from each of the sequence of steps involved in obtaining and interpreting an XPS analysis. More complex decisions, however, require the use of many pieces of information and it is here that a rule base for an expert system becomes of paramount importance. It is to be hoped that the adoption of a wizard-based system would remove some of the mystique from knowledge-based systems and inspire more experts to codify their knowledge into a form that might be used by data system designers.

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