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# Developments in expert systems for automatic examination of samples by X-ray photoelectron spectroscopy

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ABSTRACT

A brief introduction establishes the need for automatic interrogation of the X-ray photoelectron spectrum (XPS) during acquisition, to provide, immediately, the type of information required by users from a wide range of disciplines in science and technology. The review of progress in achieving this shows that progress has been made in demonstrating the use of simple Rules to extract useful information from the survey scan and to manipulate this to, for example, estimate contamination and film thicknesses on a surface. However it is argued that the essential next step is to establish a data base of the information that users from the differing fields expect to obtain from their use of XPS. Some examples of what the information might be is given for a number of fields such as Adhesion Science, Catalyst surfaces, and Bio-Systems. It is suggested that this list should be greatly expanded to provide the information in the form of Goals, each representing a relatively small step in interpretation of the data so as to achieve the required characterisation of the surface. Finally an example is given, by way of verification of a Rule base for metals and alloys, of how information in the survey scan compares with that obtained from curve fitted, high resolution, scans through individual peaks.

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## 1. Introduction

Ten years have passed since Castle and Baker published, in this Journal, “The Feasibility of an XPS Expert System Demonstrated by A Rule Set for Carbon Contamination” [1]. It is thus particularly appropriate, as well as a pleasure, to offer an updated view of ‘Expert Systems’ in this anniversary issue. Elements of rule-based expertise are now found in all modern data systems used to analyse the spectra obtained by X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). For example: peak search and identification routines assign a probability factor to elements to avoid some of the laughable mislabelling that marred earlier versions of such software whilst automatic location of peak positions builds on the security of ISO standards for finding a peak maximum. These and the many other welcome improvements in data handling deliver a fully quantitative analysis with ease. What then is the case for going further? To answer this we need to put ourselves in the position of the client, who generally provides the need for electron spectroscopy in the first place. The client needs information – not the surface analysis. Fig. 1 illustrates the relationship between these two aspects.

Typically the route to information is established in a ‘surgery’ session: a pre-analysis question and answer interview in which the analyst attempts to understand the requirements of the client and advises how these might best be achieved. This is a process that is expensive in its use of ‘expert’ time (for both parties) and provides a crucial bottleneck in the supply of analytical services. Most often the requirements suggested are not novel: for a given area of technology the analyst will have heard them before and in fact the literature for the use of XPS in technologies will confirm the, quite appropriate, repetitive nature of the surface characteristics required in a given field of technology. Given this it is usually possible for an analyst familiar with the field of technology to list the requirements in a sequence of goals to be attained in order to complete the analysis and thus write a report that fully satisfies the client. Returning to the case for going further in developing an expert system operating within the data system of an instrument: it is to incorporate the more usual of the goals so that the client sees, on screen in real time, the nature of the *information* that is being exposed during the analysis. Fig. 2 shows the separate steps that are needed to achieve this and in this review we will consider the progress that has been made in each aspect, loosely following the components of this figure.

## 2. The Goals

It is perhaps not obvious why the creation of an expert system should start with the setting of goals nor even how they should be defined. They are not the ultimate goals for the discipline –

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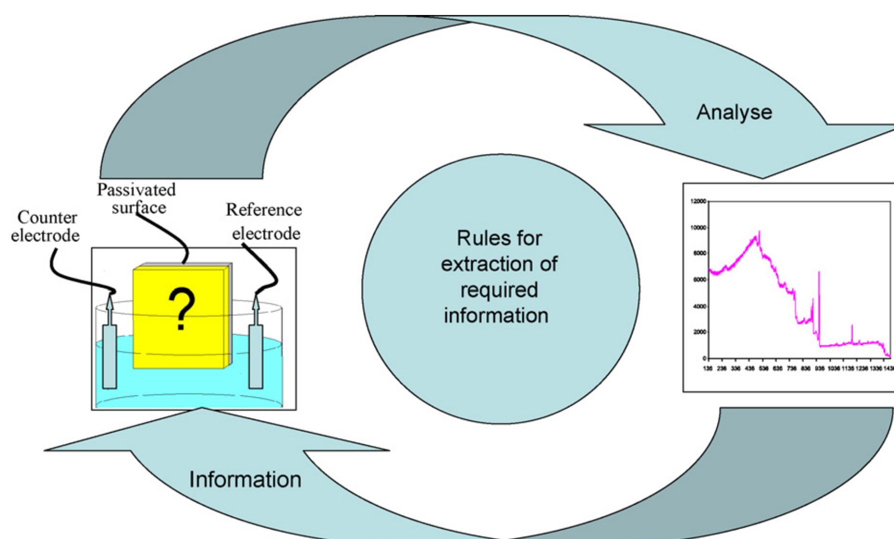



**Fig. 1.** Transforming an analysis into information for the client (here considered to be an electrochemist).

e.g. how to prevent corrosion in all metals! Rather, they are the series of steps leading to a reasonable outcome for the analytical investigation. Thus they rest heavily on the collective experience of analysts who have worked in the given area of science or technology. For example, the ultimate goal for a client wishing to examine the surface of an alloy after exposure to a given atmosphere might be expressed as 'characterising the surface layer'. Thus would then be broken down into what is achievable by XPS: probably, the surface analysis; the probable stoichiometry of the likely chemical constituents; the level of enrichment of one element or another in the surface layer; an estimate of the film thickness; etc. The establishment of goals for a given analysis is not trivial and, in discussion with a subject expert who is a newcomer to XPS it is often found that the goals initially specified maybe inappropriate to XPS, may be too time-consuming to be within budget, or might fall short of what can be easily achieved. Even in 'non-automatic' acquisition and interpretation of an analysis the establishment of clear goals for the work is important: they give a means of costing the work and negate the need for subsequent interaction with a client on the meaning of analytical results. For an 'automatic' system of analysis, well defined goals are imperative since they enable a successful stage in the process to be recognised and reported. Whilst it is recognised that there will always be very specific goals that require a high level of understanding and interaction between analyst and client, there will be others that are almost universal to the given discipline. Recognising those in the latter category and grouping them in modules, pertaining to given disciplines, is the first step in achieving autonomous supply of information from a spectrometer. These specially defined Goals will be capitalised in this review.

In their paper on carbon contamination Castle and Baker [1] identified Goals in recognising contamination as an adventitious surface layer and in estimating its thickness and thus correcting a spectrum for its influence. Subsequently Castle [2] identified the series of Goals satisfying the needs of a corrosion scientist studying electrochemical passivation of metals. In this first step in creating real-time supply of information the emphasis was given to what might be achieved from a survey scan. In some cases this will be all that is necessary, in many others the acquisition and interactive interpretation of high resolution detail scans through individual peaks will be necessary. However, even when detail scans are necessary, real-time information from the survey scan will enable a more cost-effective use of the spectrometer. A putative listing of Goals for a variety of disciplines is given in Table 1. Whilst this is by no means complete, it provides the reader with some idea of the scope of Goals that can be achieved using a survey scan alone. It is anticipated that cooperation between experts within the auspices of an ISO TC201 Working Party will enable the list to be extended and developed. It will be noticed that many goals are basic to the requirements of workers in different fields and efforts to insert these within a typical data system would reap large rewards.

Examples of Goals drawn from Table 1 might be: the probable film thickness in analysis of thin films on metals; the thickness of a contamination film; or the presence of transfer films in studies of adhesion or tribology. To achieve this first step in the development of data systems there needs to be agreement on the utility and validity of the Goals appropriate to a given user science or technology.

The publication by Castle and Baker illustrated the rules by which the first, all embracing, Goals of Table 1, identification of carbon as contamination and correction of its influence, could be achieved. Vegh [3] inserted these rules in his stand-alone data analysis system [4] and in doing so has given an excellent discussion of the associated problems of implementing rules in an expert system embedded within data acquisition software. Smith [5] checked, and found satisfactory, the suggestion that a reasonable estimate of contamination layer thickness can be obtained directly from the proportion of carbon in the overall analysis and finally Lea et al. [6] have enabled this in real-time analysis. This, latest, development is important since it illustrates the potential value of rapidly exporting acquired data to a stand-alone data system running an expert system for real-time appraisal of the survey spectra.

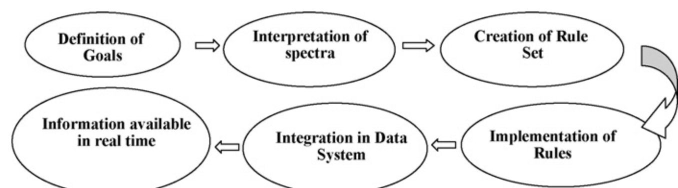



**Fig. 2.** Actions needed to achieve an Expert System capable of giving information in real time.

### 2.1. The role of goals in creation and use of an Expert System

Whilst the above account of the automation of the assessment of contamination seems like creditable progress, it has taken ten

**Table 1**
Possible Goals for different disciplines.

| Common Goals for all Disciplines | | | | |
|---|---|---|---|---|
| (1) Identify Carbon | | | | |
| (2) If contamination then estimate thickness | | | | |
| (3) Correct analysis for influence of contamination | | | | |
| (4) Report contamination thickness and corrected analysis | | | | |
| Specific Goals for different disciplines | | | | |
| **Corrosion** | **Catalysis** | **Adhesion Science** | **Tribology** | **Biomaterials** |
| Enrichment Factors | Valance state of substrate | Quality of substrate | Transfer film | Hydrophobic/hydrophilic |
| Film thickness | Presence of poisons | Hydrophobic/hydrophilic | Lubricant additives | Protein overlayers |
| Presence of hydroxide ions? | Structure | Isoelectric point of Surface | | Calcareous deposits? |
| Valence states and Film stoichiometry | Stoichiometry | Presence of weak boundary layer | | |
| Depletion or Enrichment of metal interface | Surface films | Presence of adhesion promoters | | |
| Inhibitors or accelerators of corrosion? | | Transfer film evident | | |
| | | Adhesive or cohesive failure | | |

years to achieve an outcome that was suggested as desirable by Wagner in 1975 [7]. The underlying reason for the delay appears to be the worry that autocorrection based on a carbon signal in the spectrum might give incorrect results for those instances when carbon is not only present as contamination but is also a constituent of the material under study – carbonate in corrosion studies, carbides in metals, biofilms in environmental samples, to name but a few examples. Castle and Baker addressed these issues in 1999, showing that contamination could be recognised as such by certain key characteristics. Moreover, this is only a specific example of the general problem of automating analysis – that the range of samples examined by XPS maybe too large and too complex for automatic extraction of information as defined by Goals. However, the ten years taken for autocorrection of contamination layers to be achieved, have also seen a large effort in understanding the strengths of XPS (and AES) and the security of relationships that might be used for real-time onward processing of the data. It will be necessary to circumscribe the situations in which realistic information can be obtained in real time but this should not hamper the creation of 'modules' for use in certain, much used, fields of XPS analysis.

Another potential problem is generic to the use of automatic information retrieval systems – that the logical chain of questions and answers arrives at an intermediate end point and cannot return to the main sequence that would have yielded the final assessment of the data available. Avoiding such traps is the province of the Knowledge Engineer and the design of inference engines to cope with the likely demands. Nevertheless there is less likely to be a problem if the Goals are defined to represent small incremental steps in the complete characterisation of a surface. The achievement of each Goal is reported but if other Goals cannot be reached or achieved with the available data then it might be reported that only a partial characterisation has been obtained and the gaps in knowledge will be listed – for example, to be filled by narrow or detail scans though individual peaks.

### 2.2. *Interaction between Goals, Rules and Acquisition Sequence*

The final problem in implementing a real-time information retrieval system based on the survey scan is the widespread use of a single pass for its acquisition. Once a pass is completed then it can be examined for relevant information – the position of C 1s and its use to correct for charging; the presence of elements for which the Auger parameter should be measured; the presence of elements for which there are two widely separated peaks, the slopes of the energy-loss backgrounds; etc. In a conventional acquisition sequence these will all be examined, if at all, during acquisition of the narrow scans around major peaks of selected elements. The information available, then, has been of no help in setting up these narrow scans! This problem is neatly circumvented by adopting a suggestion made by the Theme C group in the Report of the IUVSTA WP34 [8,9] workshop: that the survey scan be acquired in multiple passes, as conventionally used for the narrow scans. The first scan allows correction of the binding energy scale for charging and identification of the elements present. Windows for determination of data as required by the Rule Base can then be set for the subsequent passes which steadily improve the signal/noise ratio. In the context of information retrieval this small change is of tremendous significance since acquisition can then be terminated, not as usual when the *analysis* is of a desired standard but when the *information* is of a desired standard. For example, with each pass the contamination film thickness can be measured, as can the carbon-oxygen peak separation (to distinguish oxide and hydroxide), or the copper Auger parameter (to distinguish copper metal and copper(I) oxide). Once these values have settled to constant values within the desired accuracy the scans can be terminated. In the following discussion it is assumed that multipass acquisition of a survey scan as specified in Ref. [9] is utilised as a route to achieving the specified Goals.

### 2.3. *Identifying the 'Goals'*

To be useful in a given discipline the Goals need to be well defined and to represent small achievable and useful steps in building up the body of information needed by the client. As said earlier, the Goals define when something has been achieved – to the computer they indicate when something is known to a desired certainty and is available for use in achieving other Goals. The setting of a series of Goals need a degree of careful, sometimes introspective, consideration, even by those very familiar with the use of XPS for such a technology. The problem, in the context of the equipment manufacturer, is that the requirement to identify achievable Goals moves outside of the domain of electron spectroscopy. There are three relevant communities to consider. Firstly there are the 'Experts', the specialist users and developers of electron spectrometers who play a key role in validating the data and the manner in which it can be manipulated; secondly, there are the analysts, in Centres and Corporate Laboratories who will have to make the expert system work and thus decide if it is of value in their work and worth buying; and, thirdly, there are the clients from the huge array of engineering- and science-based industries who will discover whether the expert system improves their experience, and the cost-effectiveness, of any spectroscopy carried out on their behalf. Throughout all groups there will be found those who are specialists in disciplines, such as corrosion, microelectronics, or adhesion science and it is their knowledge which is needed to provide the target Goals.

## 3. The wide range of topics for XPS analysis

There have been the three IUVSTA workshops on the relationship between analysis based on electron spectroscopy and the information that can be derived from it [9–11]. IUVSTA Workshop 34 [8,9], in particular, contained representatives of the three communities interested in development of methods for extracting information from spectra: the client sciences; the analysts; and the manufacturers and suppliers of standalone data systems. Members of the Working Groups dealing with particular Themes within the Workshop were thus able to address issues ranging across the veracity of the data and its interpretation and the utility of the expert system concept in the user laboratory. Theme B [8] focussed on the requirements of a very wide range of user technologies, identifying the typical physical characteristics of samples and the type of information that might be obtained by electron spectroscopy. Fig. 3 based on the report of this Theme gives an indication of the wide variety of materials types and their differing forms that are presented for analysis. It is considered possible the all Forms and Types of materials listed here could be amenable to analysis within an autonomous system for extraction of the information required by most clients for XPS.

## 4. The Rule Set

### 4.1. Groundwork in the development of Rule Sets

It is one thing to make this case for an Expert System it is quite another to create the Rule Set by which the Goals might be achieved. The three IUVSTA Workshops, with their agreement on the value of particular interpretations of the spectra, makes possible the incorporation of on-screen help. A possible route to this has been explored by the author [12]. However, following IUVSTA WP 34, the author accepted the challenge of demonstrating of how the survey scan could go beyond offering help and actually provide, automatically, answers to specified goals. As an example, the Goals were specified as those required in the characterisation of passivating films on metallic surfaces [2]. The Rule Set eventually created to achieve these ran to more than a hundred separate Rules. They can be explored in the publication [2]. It is possible that these Rules, already published, enable extraction of virtually all of the useful information available in the survey scan of a single surface but more Rules will need to be specified to enable comparison of the spectrum with that of another specimen, for example when examining the locus of failure in adhesion science.

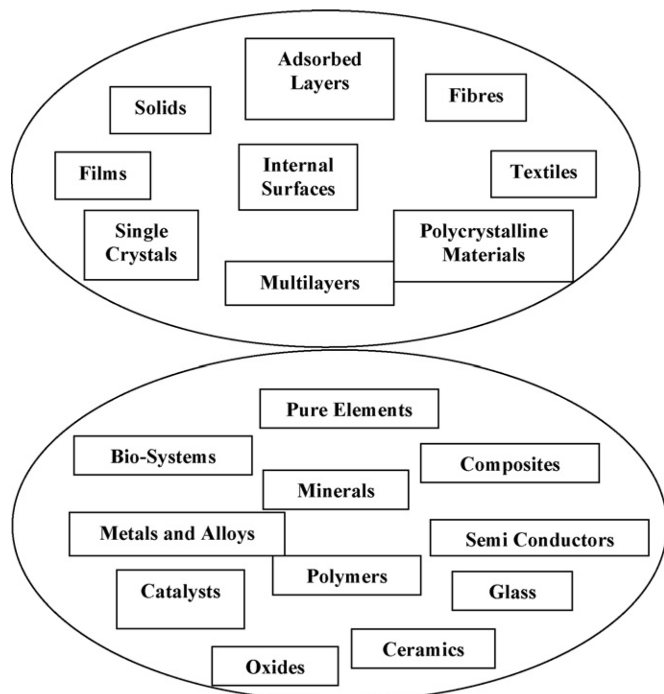



**Fig. 3.** Upper, Forms of Materials offered for Analysis; Lower, Types of Material offered for analysis.

### 4.2. Writing Rules

When an expert analysts first examines a survey scan he or she will make use of information about the sample. If it is a metal then the peaks will not be shifted far from position by electrostatic charging – so the client will be asked if the sample is a metal. It is known that many elements, especially Cr, form carbides on ion etching – so, has it been etched? This may influence to position of the carbon 1s peak. What kind of atmosphere has it been exposed to? The answer to this will indicate whether a hydroxide in likely to have formed. These and similar questions imply that a useful automatic system will need to communicate with a sample descriptor that is input to the data system. Each of the 'Materials Types' listed in the ellipse of Fig. 2 has a set of attributes (conducting, non-conducting; contains carbon; is a thin film on silicon; etc.) which set up a prior understanding of the sample and which will be useful in interpretation. Such a concept is outlined in a little more detail in Ref. [9].

An expert will also cast an eye over features other than the major peaks for given elements that are normally used for quantification. If the chromium 2p peaks are present then the 3p peak may also be looked at to quickly assess its intensity in relation to that of the 2p and to other elements in the spectrum – the point being that the two peaks correspond to significantly different kinetic energies and thus to different depths of analysis. Whether or not this is useful depends on the separation in binding energy of the chosen peaks and this will restrict the number of elements for which it can be used. Other elements will have useful, well resolved Auger electron peaks, or will have satellites associated with particular valance states. For such 'expert' information to be available to the computer a new form of look-up table is required. A suggested form of such a table is reproduced in Table 2 and described in more detail in Ref. [2]. A spectroscopist will probably undertake an 'instant' assessment of the behaviour of the energy-loss background associated with particular peaks – does it slope up or down? Or is it sloping more or less in relation to other elements? This will give a view about the behaviour of near-surface concentration gradients. Finally, this expert will look for agreement between the various signs, in the spectrum, that point to a likely surface composition and structure: a consensus will be required between the result of any Rules that are written. Thus, the need in establishing an expert system is to write and validate Rules which make use of all of this information to characterise the surface in a manner that is meaningful to a client.

In the various publications cited above, the author has taken the view that the crucial activity in writing Rules is to make the interpretation of the spectrum available to the Knowledge Engineer who is setting up the expert system or is integrating elements of expertise into the acquisition software. Thus, the Rules are written as If . . . Then statements, that are as far as possible self-explanatory.

For example:

$$\begin{aligned}&\text{If Carbon-Contamination is Yes}\\&\text{then}\\&\text{Carbon_Thickness_1 is } -\lambda_c \cos\theta \ln(1-\text{Carbon_Fraction})\end{aligned} \tag{1}$$

where $\lambda_C$ is the inelastic mean free path IMFP of the C 1s photoelectron in the contamination layer, and $\theta$ is the emission angle relative to the sample normal.

**Table 2**
A listing of useful secondary features in the spectra of representative elements with position in the spectrum and an indication.

| Z | | Low KE Peak (BE, eV) | High KE Peak (BE, eV) | Auger peak (KE, eV) | Satellites (BE, eV) |
|---|---|---|---|---|---|
| 6 | C | 1s: 285 | | KLL: 260 | |
| 7 | N | 1s: 398 | | KLL: 378 | |
| 8 | O | 1s: 531 | | KLL: 510 | |
| 9 | F | 1s: 685 | | KLL: 655 | |
| 11 | Na | 1s: 1071.5 | 2s: 64 | KLL: 994 | |
| 12 | Mg | 1s: 1305 | 2s: 90 | KLL: 1185 | |
| 13 | Al | 2p: 73 | | KLL: 1393.3 | |
| 14 | Si | 2p: 102 | | KLL: 1616.5 | |
| 15 | P | 2p: 133 | | | |
| 16 | S | 2p: 164 | | | |
| 17 | Cl | 2p: 199 | | | |
| 20 | Ca | 2p: 347 | | | |
| 24 | Cr | 2p: 574.1 | 3p: 45 | LMV: 1101.5 | Cr III: 597 |
| 25 | Mn | 2p: 639 | 3p: 49 | | |
| 26 | Fe | 2p: 706.8 | 3p: 55 | LVV: 702.4 | Fe II: 729, Fe III: 733 |
| 27 | Co | 2p: 778 | 3p: 62 | LVV: 773 | Co II: 787, 804 |
| 28 | Ni | 2p: 852.3 | 3p: 68 | LVV: 846 | Ni II: 861, 879 |
| 29 | Cu | 2p: 932.5 | 3p: 78 | LMM: 918 | Cu II: 942, 961 |
| 30 | Zn | 2p: 1021.5 | 3p: 90 | LMM: 992 | |
| 31 | Ga | 2p: 1117 | 3d: 18.5 | LMM: 1068 | |
| 32 | Ge | 2p: 1219 | 3d: 28.95 | LMM: 1145 | |
| 33 | As | 2p: 1326 | 3d: 41.4 | LMM: 1225 | |
| 34 | Se | 3d: 55.3 | | LMM: 1302 | |
| 46 | Pd | 3d: 335 | | MMM: 327.8 | |
| 47 | Ag | 3d: 368 | | MMM: 357.8 | |
| 48 | Cd | 3d: 404.8 | | MNN: 384 | |
| 49 | In | 3d: 443.6 | 4d: 19 | MNN: 410 | |
| 50 | Sn | 3d: 484.6 | 4d: 25 | MNN: 437.3 | |
| 51 | Sb | 3d: 528 | 4d: 34 | MNN: 464.5 | |
| 52 | Te | 3d: 572.7 | 4d: 44 | MNN: 492.1 | |
| 78 | Pt | 4p: 521 | 4f: 70.9 | | |
| 79 | Au | 4p: 547 | 4f: 83.8 | | |
| 80 | Hg | 4p: 577 | 4f: 99.7 | | |
| 82 | Pb | 4p: 645 | 4f: 136.6 | | |

This table is an illustration of the wider range of information that will be need for implementation of an automated system for analysis of the Survey Scan. It forms the basis for the windows set in the present work and as a guide for others to augment as may be necessary or useful.

The first line of this statement indicates that there is a contamination film containing carbon on the surface. This conclusion is reached by applying several rules concerning the spectrum features of the carbon peaks and also from the input knowledge that the sample had been exposed to an environment known to give surface contamination. The Knowledge Engineer designing the system is then given a simple relationship that has been tested by the user community, to enable the contamination layer to be expressed as a thickness. The full set of Rules to validate this statement can be found in Ref. [2].

Knowledge of the thickness of the contamination layer enables the measured intensities to be corrected, i.e.

$$I_{\mathrm{Z,corrected}} = I_{\mathrm{Z,measured}} \mathrm{Exp}(\mathrm{Carbon_Thickness_1}/\lambda_Z \cos\theta) \quad (2)$$

This is the stage reached by Baer et al. as described in their presentation at AVS 55 [6].

The test for the electron spectroscopist is to see how much specialised knowledge or rule-of-thumb estimates can be written in the form of such simple rules and thus made available for validation and eventual incorporation in data systems. It is helpful to look at the richness of information in a survey scan taking an actual survey scan of passivated stainless steel as an example (Fig. 4). Looking at Fig. 4 we quickly see that the expected components of stainless steel are present – this may seem trivial but in some cases such a quick view will establish that the correct side of the sample was mounted for examination, or, indeed, that the sample had not fallen off the mounting stub. We might also notice that the Fe 3p peak is greater in magnitude than the Cr 3p whereas the reverse is true for the equivalent 2p peaks: a sign of a surface enrichment of Cr. We also notice, in confirmation, of the enrichment of Cr, that the background slope for Fe is negative with respect to the binding energy axis but for Cr it is positive: Cr increases in concentration towards the surface whilst Fe decreases in concentration. We realise there are some key intervals to measure and that satellites, present or absent, will give an indication of the presence of certain common oxides. All of this information would take much time to process for an individual spectrum but if Rules for the required processing steps were established in a computer the outcome could be available on screen as soon as counts for the final channel have been registered.

The Rules for such an analysis to be obtained are given in [2] and the complete characterisation of a similar spectrum reached the conclusions given in Fig. 5. Note that this information would be shown on screen in real time and be updated as each scan was completed. The Rules by which this information was obtained mix the many aspects of XPS, both quantitative and qualitative with aspects of the sample that are already known. For example the enrichment factors compare the surface analysis with the bulk analysis, perhaps known from EDX analysis or from the nominal composition of the alloy. The conclusion is supported by the 2p/3p intensity ratio of the elements and by the behaviour of the energy loss backgrounds. Likewise, the conclusion that $OH^-$ ions form a major component of the chemical make up of the surface layer comes from the position of the oxygen peak relative to the carbon 1s and is supported by a calculation of the electroneutrality requirement using a prior knowledge of the likely valance states of the metal ions. Thus every conclusion is mutually supported, often using knowledge that is adjunct to the spectroscopy itself. The expert community should be encouraged to publish, in the form of Rules, every new method that is discovered to give useful information from the survey scan. This will increase the scope for mutual support between multiple routes for achieving Goals. However, reaching a conclusion by multiple routes brings with it the problem of how a consen-

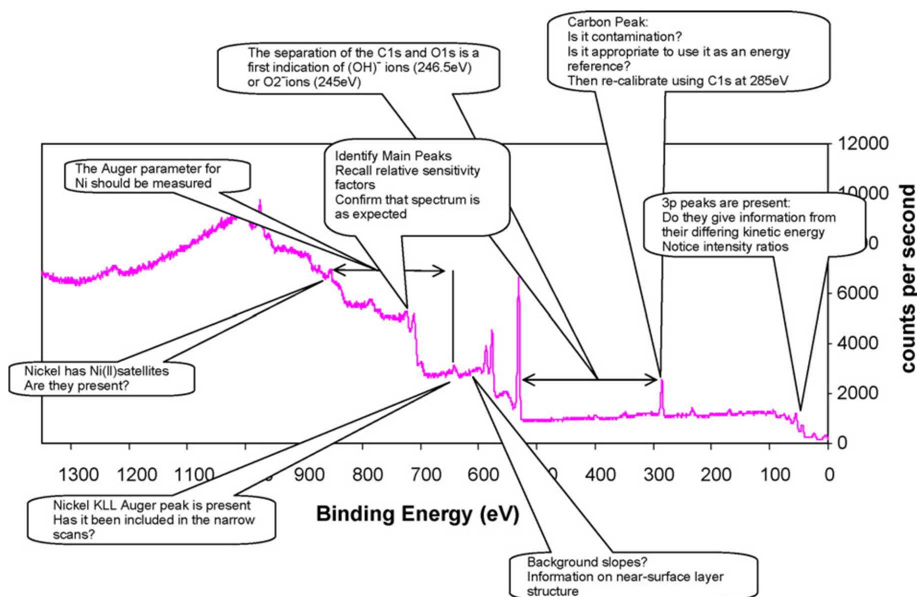


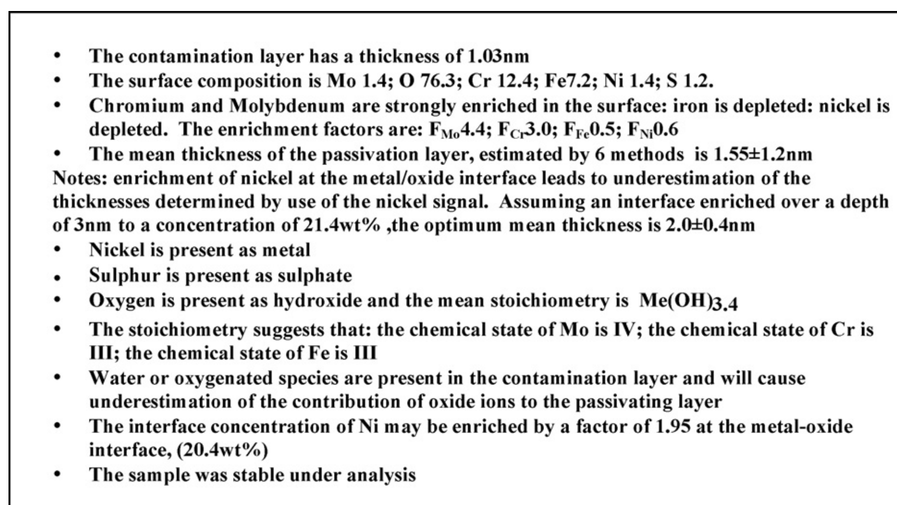

**Fig. 4.** Comments on significant features conveying information in a survey scan.

sus is to be reached in order to give an outcome with the best validity.

*4.3. Consensus in information*

The problem of consensus has two forms in the rule base for electron spectroscopy. There are conclusions reached by application of heuristic rules, i.e. qualitative rules based on observation or good practice and those rules which reach a quantitative conclusion. In the Rule Set used in the example of a 'Module for Corrosion Science' consensus is treated differently in the two classes of rule. The conclusion that carbon is present as contamination is reached on the basis of heuristic rules, e.g. it is not expected to be present in the material being examined; C 1s has a peak shape typical of adsorbed material (value of the Shirley scattering parameter); the C KVV Auger peak has a shape characteristic of $sp^3$ co-ordination (separation of the maximum and minimum peaks in the differentiated spectrum); the C 1s–O 1s interval in kinetic energy is within a range expected for aliphatic compounds (difference in kinetic energy); and the energy-loss background for the C 1s peak is that expected for a thin surface layer (value of slope). Although some of these qualitative assessments are based on the value of a number derived from the spectrum the result is a simple binary, Yes (the number is in range) or No (is outside the range). In the Module a confidence value was assigned to each of the above tests for contamination. The default value was set at 20% for each Yes, i.e. if the carbon was $sp^3$ then we can be 20% certain that it is present as contamination. By making the confidence test additive then each test that is passed contributes a further 20%. If the goal post is set at 80% then four positive answers enable the Goal to be achieved. There are many possible variations of this, for example, a No answer might lead to 20% being deducted. The contribution that needs to be made by the spectroscopist is to give better, more realistic, values for the confidence level associated with the tests being applied.

More sophisticated assessment of the outcome of tests use a Baysean [13] approach to assess whether a conclusion is 'correct'. In this the history is important. For example the more often contamination is found on samples in XPS the greater the certainty that any one of the measurements used to identify contamination is reliable. In fact, this is what gives spectroscopists the certainty



- The contamination layer has a thickness of 1.03nm
- The surface composition is Mo 1.4; O 76.3; Cr 12.4; Fe7.2; Ni 1.4; S 1.2.
- Chromium and Molybdenum are strongly enriched in the surface: iron is depleted: nickel is depleted. The enrichment factors are: $F_{Mo}$4.4; $F_{Cr}$3.0; $F_{Fe}$0.5; $F_{Ni}$0.6
- The mean thickness of the passivation layer, estimated by 6 methods is 1.55±1.2nm

Notes: enrichment of nickel at the metal/oxide interface leads to underestimation of the thicknesses determined by use of the nickel signal. Assuming an interface enriched over a depth of 3nm to a concentration of 21.4wt% ,the optimum mean thickness is 2.0±0.4nm

- Nickel is present as metal
- Sulphur is present as sulphate
- Oxygen is present as hydroxide and the mean stoichiometry is $Me(OH)_{3.4}$
- The stoichiometry suggests that: the chemical state of Mo is IV; the chemical state of Cr is III; the chemical state of Fe is III
- Water or oxygenated species are present in the contamination layer and will cause underestimation of the contribution of oxide ions to the passivating layer
- The interface concentration of Ni may be enriched by a factor of 1.95 at the metal-oxide interface, (20.4wt%)
- The sample was stable under analysis

**Fig. 5.** The information that could be available on screen in real time by a rule-based interpretation of the survey scan.

that a C 1s peak on a sample, that is unlikely to contain carbon, is because of contamination.

An example of the use of quantitative rules can be seen in the measurements of film thickness. The thickness can be determined by attenuation of nickel in the steel since this is not present in the oxide, or by the 2p/3p ratio, or by assessing the magnitude of the energy-loss tail in relation to the peak area, etc. In all six methods were identified and for want of a better method, the average value was taken. In a more satisfactory assessment of consensus between the values a weighted average would better reflect the differing confidence with which the individual values are endowed. Assessment of the weights to be ascribed to each method is an area in which input from the electron spectroscopy community is required. The use of *If . . . Then* rules for the information base is a simplification that may not allow for every eventuality. At the commencement of analysis none of the objects used by the rule base will have a value but are constantly being scanned to see if they can be given a value from any source – sample descriptor or spectrum. In assessing contamination the object *Carbon-Contamination* might well be set to *Yes*, even before the acquisition starts, by virtue of having been exposed to air. But, the sample might be a bio-material containing organic polymers so there is immediately a conflict between being contaminated and the inevitability of finding C 1s features in the spectrum. If this is not to lead the user down a misleading path we might need a statement that means the 'contamination' questions are not asked. But what to do with setting a value for the object, *Carbon-Contamination*? It is neither *Yes*, nor *No*, in fact it is 'Don't know'. Leaving it empty may not be an option because, depending on the inference engine used in the system, the expert system could stall whilst it tries to obtain a value for the object. Such issues have been discussed by Vegh [3,4], who concluded that more sophisticated rules capable of more than two answers is necessary in operating a satisfactory expert system. In the previous paper by the present author it was assumed that qualified *Yes* and *No* values were possible, e.g. *Carbon-Contamination* is *Yes* (20%). Setting the probability to a very low value (1%) might be the best method for indicating a 'don't know' value.

### 4.4. Interpretation of spectra

In parallel with the development of thinking concerning expert systems there have been notable developments in the interpretation of spectra in terms of near surface structure. *QUASES* [14] has been available for some fifteen years and has been under continuous development to reveal more facets of structure throughout this time. The near surface structure is extracted by fitting peaks to the expected intensity distribution taking into account the information depth as a function of kinetic energy and relating this to the observed shape of the energy loss background in the vicinity of the peak. It relies on interactive input and optimisation of trial structures and element distribution within them. SESSA [15], is based on the creation of a matching spectrum by manipulation of near surface concentration gradients. Both of these analytical techniques rely on expert modelling of possible physical structures. By contrast the present concept of an expert appraisal of the spectrum enables a model to be derived from the spectrum without preconceptions. It would thus make an excellent starting point for further iterations within the QUASES or SESSA programs.

## 5. Validating the outcomes: an example

As an example of the ability to extract information concerning a set of unknown surfaces, the influence of low (ambient) temperature oxidation on the surface composition of a set of copper-nickel alloys was examined [16]. In each case the set was also characterised using narrow scans by the traditional means of data analysis by curve-fitting. Table 3 gives: the composition of the alloys studied; the set of four treatments they were given before analysis and a set of five Goals required: in all ninety-five pieces of information will be generated by the analysis.

**Table 3**
Six metals and alloys were given four treatments and the data analysed to yield five Goals.

| Alloy | Treatments | Goals |
|---|---|---|
| Ni | | Presence of contamination by organic molecules and thickness of the contamination layer |
| Cu30Ni70 | 30 s etching | The corrected, mean, composition of the probed depth |
| Cu70Ni30 | As received | Enrichment factors, relating the mean elemental composition of the surface layers to the known composition of the alloy |
| Cu80Ni20 | 24 h 100 °C oven | The presence and thickness of an oxide or similar layer |
| Cu85Ni15 | 24 h 100 °C oven then 30 s etching | The valence state of all oxidized species and a possible stoichiometry |
| Cu | | |

If undertaken in the conventional way of using narrow scans to acquire the composition and then curve-fitting in order to estimate film thickness, it would be accepted that this is a considerable project. It was, therefore, a reasonable test to establish whether (a) the required Goals could be met using the survey scans alone, and (b) whether the conclusions reached were supported by the more rigorous method of using narrow scans.

Fig. 6 gives the wide scan spectra obtained from the 30/70 Cu/Ni alloy after exposure. These spectra are shown in the form of a sequence of aggregated and averaged scans, from 1 to 10. The Survey Scan used the 'St Malo' format, i.e. 0–1350 eV in 0.4 steps. The acquisition time was 10 ms per step given a total elapsed time for the 10 scans of 35 min. The analysis time was the same as normally used in the single-pass survey scan and the difference is because

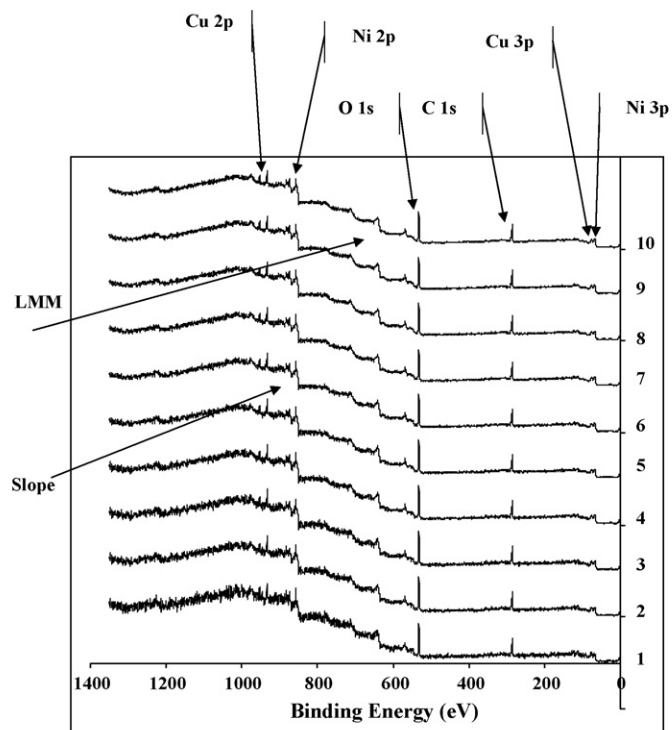



**Fig. 6.** The Analysis of 70Cu30Ni copper–nickel alloy carrying the as received oxide film: acquisition following the protocol suggested in UVISTA-WP34.

**Table 4**
Regions selected for examination of Cu/Ni alloys.

| Element | Type | Measure area & quantify | Obtain position | Obtain slope |
|---|---|---|---|---|
| Carbon | 1s | √ | √ | |
| Carbon | 1s background | | | √ |
| Carbon | KLL | | √ | |
| Oxygen | 1s | √ | √ | |
| Oxygen | 1s background | | | √ |
| Nickel | 2p | √ | √ | |
| Nickel | 3p | √ | | |
| Nickel | 2p background | | | √ |
| Nickel | LVV | | √ | |
| Nickel | 2p satellite | | √ | |
| Copper | 2p | √ | √ | |
| Copper | 3p | √ | | |
| Copper | 2p background | | | √ |
| Copper | 2p satellite | | √ | |
| Copper | LMM | | √ | |

of the settle time allowed between scans, which for a range of 1350 eV, is large. In setting the windows to be examined in the survey scan the information given in Table 2 is used. Both copper and nickel have useful peaks at a greater kinetic energy than the 2p peaks conventionally used for quantification, so windows will be set around these; both peaks also have Auger peaks and satellites giving useful information. Table 4 shows these and other relevant windows that will be automatically set. There may be no need to call on all the information provided by these windows and the results derived from them, but if a Rule is fired that needs input, then it can be found in the system. The window setting depends only on those regions required by the look-up table for the elements expected to be present. The Goals by contrast are determined by the requirements of the subject science or technology, as set out in the examples given in Table 1. In the case of thin native oxide films on metals these would be:

- Goal_1 the presence and thickness of any contamination layer;
- Goal_2 the, corrected, mean composition of the probed depth;
- Goal_3 enrichment factors, relating the mean, elemental, composition of the surface layers to the known composition of the alloy;
- Goal_4 the presence and thickness of an oxide or similar layer;
- Goal_5 the valence state of all oxidized species, a possible stoichiometry;

For each alloy, pure metal and surface treatment, the system then would work through the Goals needed to provide the required surface 'characterisation'. Carbon is identified as contamination and the thickness implied by the carbon peak area is used to correct for its attenuation. Goal_1 and Goal_2 are achieved. The contamination layer thickness and the corrected quantification would then be displayed on screen during analysis.

In Table 5 the analyses derived from the survey scans are compared to the values obtained from the narrow scans of the individual elements in the conventional manner. The analyses for the fifth and tenth scans are given to illustrate the fact that the results obtained by aggregating each additional pass of the survey scan rapidly reach a stable value. This shows that if the precision of the analysis was used to terminate the acquisition, then fewer passes would be used. There is also good agreement between the values from the survey scan and from the narrow scans. This agreement is perhaps no surprise but, the important consequence is that it validates the correction for attenuation by a contamination layer whilst acquisition is under way.

Goal_3 is readily achieved if the sample descriptor can be interrogated in real time to ascertain the nominal composition of the alloys. Again this can be shown on screen and updated as each pass is made. The enrichment factors obtained in this manner are shown in Fig. 7 for the whole set of samples and treatments. The smaller inset figure shows the values obtained from the narrow scans. Briefly, we see from this plot that at room temperature there is a relatively strong excess of nickel in the surface film across the whole range of compositions. By contrast, after 24 h exposure at 100 °C, the enrichment of nickel is replaced by an enrichment of copper in the high copper alloys. This behaviour is better defined by the measurements made using the narrow scans but there is no essential difference in the conclusions reached from the survey scans alone. The cross-over in behaviour occurs at ca. 50 at.%. The 30 s etch brings both surfaces back to a similar slightly Ni-rich composition. The grid of lines shown on this diagram, annotated from 0.2 to 5.0 is described as an enrichment rank in work by Castle and Asami [17].

Goal_4: The thickness of a surface film is normally assessed by peak fitting of a peak that shows multiple chemical states in order to obtain a ratio of the intensities of the surface and bulk components and is undertaken after the completion of the analysis. In the case of copper compounds there is an additional difficulty because of the lack of significant chemical shift in the formation of Cu(I) oxide and similar compounds. However the thickness of a surface layer can be estimated using the near surface concentration gradient obtained from the relative intensities of the 2p and 3p peaks for copper and also for nickel. The Rule sequences for this are derived in Ref. [2] and are based on the fact that the XPS value (a surface biased average of the concentration within the depth of analysis) will be equal to the actual value at some depth beneath the surface. These depths will be different for the values derived from the 2p and the 3p peaks, respectively, and thus, if they were known, could be used to estimate the value and direction of any concentration gradients. Seah et al. [18], have shown that when the XPS concentration is placed at a depth of 0.35*t*, where *t* is the thickness of a layer containing the elements concerned, then the observed concentration is almost invariant with angle and this depth has been adopted in the published Rules as the point at which the actual concentration is known. For the purpose of providing an estimate of the thickness of an altered surface region t has been given the value of 3λ, the effective depth of analysis in XPS.

As seen from the survey scans provided for the 70Cu/30Ni alloy, there are no satellites associated with the copper 2p peaks. This was true for all samples examined showing that any copper oxide is in the Cu(I) state. Thus the oxide and metal intensities cannot be separated and the oxide thickness cannot be obtained by the more traditional means of curve fitting. The nickel peaks, however, can be fitted for metal and oxide components and an estimate for film thickness based on fitting the narrow scan peak is obtained by the usual methods. The results obtained from the nickel-rich 30Cu70Ni alloy using the 2p and 3p peaks for both Cu and Ni together with the value obtained from the intensity of NiO are given in Table 6. The agreement between survey and narrow scans appears reasonable and has the benefit of being obtained by three independent methods.

Goal_5: Determination of the possible chemical composition of a surface film relies heavily on the identification of the valance state of the metallic species. In the case of copper there is no shake-up satellite visible in the survey scan – which could be recognised automatically by the use of peak recognition software using the expected position of the satellite given in the look-up table (Table 1). Thus the copper is in the metallic or Cu(I) state. Automatic retrieval of the Auger parameter identified Cu(I) as the major component. The major peak for nickel is in the Ni(II) position. The separation of the C 1s and O 1s peaks in the as received sample is 246.8 eV which indicates (ref 2, Rule 88) that $OH^-$ ions are a major component of the surface film. All of this information is readily obtained

**Table 5**
Surface compositions (at.%) determined after 5 scans, 10 scans or by data from narrow scans (ns).

| 70/30 Cu/Ni | 30 s ion etch | | | Air formed film | | | 24 h at 100 °C | | | 24 h at 100 °C + 30 s ion etch | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 5 scans | 10 scans | ns | 5 scans | 10 scans | ns | 5 scans | 10 scans | ns | 5 scans | 10 scans | ns |
| O | 11 | 9 | 12 | 67 | 68 | 72 | 74 | 72.5 | 78 | 59 | 59 | 61 |
| Cu | 58 | 59 | 57.5 | 15 | 16 | 12 | 21.5 | 21 | 17.5 | 29 | 28 | 26 |
| Ni | 30 | 32 | 30 | 12 | 13 | 12 | 3 | 5 | 4 | 11 | 12 | 11 |
| N | 1 | 0 | 0.5 | 6 | 3 | 4 | 1.5 | 1.5 | 0.5 | 1 | 1 | 2 |

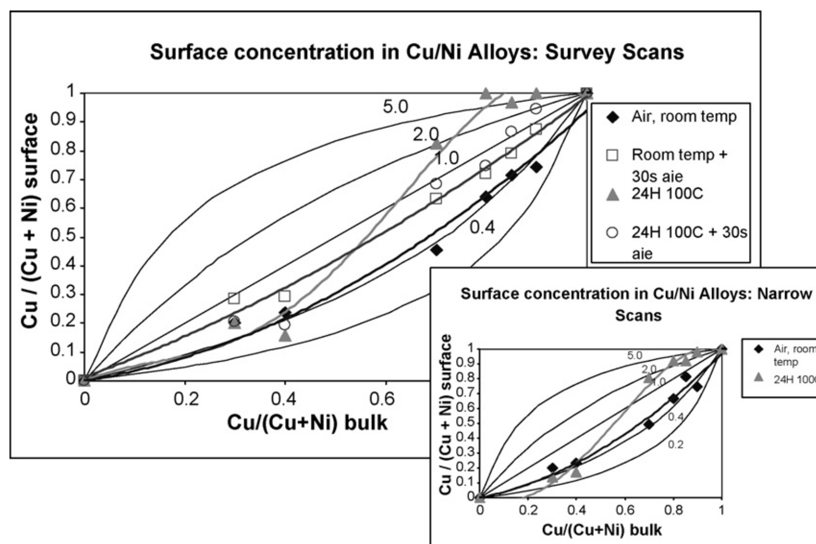



**Fig. 7.** Comparison between surface and bulk analysis of Cu/Ni alloys, as obtained by survey and narrow scans.

**Table 6**
Estimated film thickness as obtained from survey and narrow scans (ns).

| 30/70CuNi as received film thickness (nm) | | | 30/70CuNi 24 h 100 °C film thickness (nm) | | |
|---|---|---|---|---|---|
| Cu 2p/Cu 3p | Ni 2p/Ni 3p | NiO/Ni (ns) | Cu 2p/Cu 3p | Ni 2p/Ni 3p | NiO/Ni (ns) |
| 0.84 | 0.93 | 0.78 | 1.01 | 0.93 | 1.11 |

by simple manipulation of the data in the survey scans using Rules already provided. The analyses given in Table 5 for the 70Cu30Ni alloy would correspond to 13% $Ni(OH)_2$ plus 8% $Cu_2(OH)_2$ and thus account for only 42% of the oxygen signal whereas the amount found is 68%. This could indicate the presence of small quantities of carbonate or sulphate and would be valuable information if reported during acquisition of the survey scan.

This example has shown how a relatively simple set of Goals can be achieved by processing during acquisition of a survey scan giving information that is likely to be of value to a client and thus to assist in the next steps to be taken. The Rule base for retrieval of the information is available in the cited Ref. [2] for many, if not most, of the Goals to be achieved for a wide range of disciplines.

## 6. Sample descriptor

The role of the sample descriptor is perhaps the most neglected of the requirements for a fully functioning expert system. It is crucial to the operation of real time interpretation of the spectra when a comparison has to be made with what the client already knows about the sample. The rules require the use of Objects to which values are attached. For example, the value of the Object 'Contamination_Thickness' can be calculated and set once the Object 'Contamination' is given the value Yes, indicating that most of the carbon in the spectrum is present as a contamination layer on the surface. The rules used to confirm that Contamination is Yes are mainly based on the spectra themselves but there are two which depends on prior knowledge of the sample, i.e. That there is no carbon in the sample and that it has been exposed to air or to water, likely to produce a contamination film. In the above example based on the Cu/Ni alloys the determination of the enrichment factors, or the production of the plotted values shown in Fig. 7, are only calculable if the bulk composition is known to the system. In other cases the comparison might be made with an earlier analysis – for example the partner side of a metal-coating failure to determine whether adhesive or cohesive failure has taken place. Thus a pre-analysis question and answer page, which duplicates much of what is discussed in a 'surgery' session before undertaking analysis in a conventional manner is what is needed. Asking the right questions is obviously facilitated by a well posed set of Goals and it is suggested that the sample-identifier interacts strongly with the prior-defined Goals for the analysis. For example, in order to establish whether failure of an adhesive bond is adhesive or cohesive it is necessary to compare the two facing sides of the failed joint. The sample descriptor called into play for use in adhesion studies must therefore ask if the sample is one face of a pair. The system would then retain the spectra and derived data for the 'A' side for comparison, during acquisition, with the spectra and data for the 'B' side.

## 7. Summary and conclusions

This review has indicated that the first step in an automatic system for interpreting the survey scan is to know what is required by

the particular client. This is no different to the interview that needs to be undertaken by the spectroscopist and the client in the real world but in the virtual world it is necessary to predefine a series of possible pieces of information, as required by a given user technology. It is suggested that these are formalised as Goals and examples are given for a number of technologies such as corrosion science, adhesion science and technology, bio-systems and tribology. This list, and the associated Goals, needs to be expanded, drawing on the expertise of surface scientists working in close association with particular user technologies.

The next step is relating a rule base to the needs of the Goals specified for each user technology. Many Rules will be common to several technologies and are already available in Ref. [2]. However there will be a need for a further extension of this set to meet the special needs of each technology. The creation and elaboration of a rule base is an introspective exercise for most workers in electron spectroscopy since it requires codification of the numerous qualitative and quantitative methods by which experienced spectroscopists reach a conclusion about the likely surface composition and structure of the surface. For this reason the Rules created need to be exposed and agreed as serving a given purpose within a required precision by the community of electron spectroscopists. Rules once defined should then be arranged as subsets to meet the Goals for each particular technology.

Finally, all of this will succeed only if the Rules draw on information that is available concerning the surface under investigation. This means that these is a need for a sample descriptor as a front end. Once again the sample descriptor will require sub-sets of information relating to particular technologies to guide the user to input the information most likely to be called on during the analysis.

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