

Invited Paper

## XPS: Issues with Data Acquisition and Data Processing

J.T. Grant

Research Institute

University of Dayton

300 College Park, Dayton OH 45469-0051, USA

[j.grant@ieee.org](mailto:j.grant@ieee.org)

(Received: November 26, 2007; Accepted: December 21, 2007)

Methods for both data acquisition and data processing are very important for analyzing samples in x-ray photoelectron spectroscopy (XPS/ESCA). I find that many users do not understand the operation of their instruments and therefore are not taking data using optimal conditions. This can be as simple as using the wrong combinations of analyzer apertures and/or pass energies, energy intervals, and even the x-ray source when more than one source is available. Sometimes, limitations for data acquisition are imposed by the acquisition software. In data processing, the analyst is often limited to the processing software provided by the instrument manufacturer. There are however, some software packages that can convert data from several (proprietary) formats into ASCII. Also, software developers are increasingly providing output of their data into the ISO format for surface analysis. This, in principle, allows one to select from a wider variety of data processing packages. Many software packages today are very powerful and provide quite a variety of processing options. This paper discusses and illustrates some basic issues with data acquisition and data processing in XPS/ESCA.

### 1. Introduction

During the past year, I have seen many examples of problems with the analysis of surfaces using x-ray photoelectron spectroscopy (XPS/ESCA). In many cases, instrument operators do not understand how the instruments acquire spectra, and therefore are not taking data using optimal conditions. Such conditions can be as basic as using the wrong combinations of analyzer apertures and/or pass energies, and using too many energy steps in spectra, particularly for survey scans. Even when more than one x-ray source is available, operators often use just one source for all their analyses. Sometimes, limitations in data acquisition are imposed by the acquisition software. Examples of this are (a) selecting from a fixed set of energy step intervals, (b) selecting from a fixed set of acquisition times (dwell times) per energy step, or (c) having to take data at only one possible dwell time per energy step. In data processing, the analyst is often limited to the processing software provided by the instrument manufacturer, sometimes because of difficulty in outputting the data into a non-proprietary format for use with other soft-

ware. Examples of this are (a) using rather poor peak identification routines where peaks are often misidentified, (b) the inability to combine chemistry information from peak fitting higher resolution spectra into a quantification table obtained from a survey scan, or (c) the inability to fix peak intensities between chemical components of different elements according to their known chemistries. There are, however, some software packages that can convert the original data from several proprietary formats into the ISO14975 and 14976 formats. Also, instrument manufacturers themselves are increasingly providing output of their data into the ISO format for surface analysis. This, in principle, allows one to select from a wider variety of data processing packages should the need arise. Many software packages today are very powerful and provide quite a variety of processing options.

This paper discusses and illustrates several basic issues with data acquisition and data processing in XPS/ESCA, using several case studies. These case studies are (a) selection of apertures and pass energies with a double-pass cylindrical mirror analyzer in order

to collect appropriate data in minimum time, (b) selection of energy step intervals for acquiring spectra with multi-channel detector systems and its impact on quantitative analysis using peak area, (c) selection of pass energies and energy step intervals in a hemispherical analyzer (HSA), again regarding the collection of appropriate data in minimum time, (d) acquisition times for appropriate signal-to-noise and detection limits, (e) a possible analyzer problem involving analyzer scattering, and (f) issues regarding the identification of peaks in spectra.

## 2. Case studies

The issues with data acquisition and data processing discussed in this paper are presented as several case studies.

### 2.1 Pass energies and apertures in a DPCMA: collecting appropriate data in minimum time

A double-pass cylindrical mirror analyzer (DPCMA) was manufactured and sold by Physical Electronics for XPS (and AES) analysis [1]. The analyzer has two sets of apertures, one being in the central region separating the “two” cylindrical analyzers that are in series, the other being at the exit of the analyzer. There are three possible apertures in each set, and these are referred to as small, medium and large. Larger apertures give more luminosity, but degrade the energy resolution.

I had used such an analyzer for several years and was familiar with its operating design. One steel research laboratory that I visited was using the same model DPCMA for their XPS work, but I was surprised with the rather poor signal-to-noise of their spectra. In checking the instrument operation with the laboratory technician, I found that he always took his XPS data using the two small aperture settings, and selected the pass energy to determine the spectral resolution. His samples were relatively large and the coatings that he was examining were uniform laterally, so this was the worse possible setting for his XPS analysis. As mentioned earlier, larger apertures give more luminosity, but degrade the energy resolution.

However, luminosity increases as the square of the aperture diameter whereas energy resolution degrades linearly with aperture diameter. Therefore in XPS

studies of uniform samples, one must use the large apertures and change the pass energy for energy resolution in order to collect appropriate data in the shortest time.

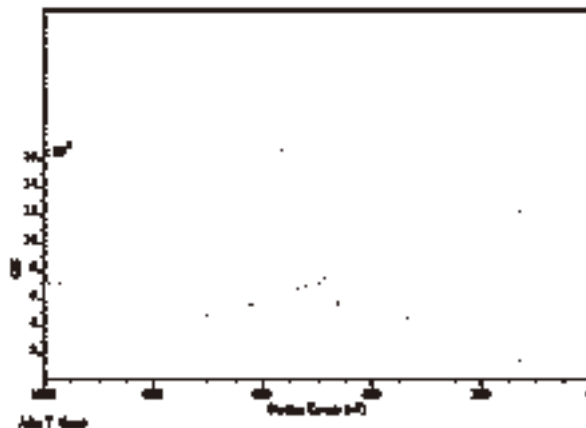


Fig. 1. An example showing a three-times improvement in signal-to-noise, as would be obtained using large-large apertures (top) rather than small-small apertures (bottom) in a DPCMA. The spectra have been offset for clarity.

By using the large apertures, the technician was able to acquire similar data ten times more quickly than before, or obtain a three-fold improvement in signal-to-noise (and detection limit) for the same acquisition time that he used for many years beforehand. An example of such an improvement is shown in Fig. 1. These spectra are displayed after converting the raw data into ISO format, as are many of the spectra presented later.

### 2.2 Energy step intervals with multi-channel detector systems: impact on quantitative analysis using peak area

Before acquiring spectra, it is important to consider what is needed from the analysis. If one is interested in obtaining peak areas for quantitative analysis, the acquisition parameters used should be quite different than if one is interested in peak lineshapes for studying chemical effects. Most XPS instruments sold today have multiple-channel energy detection [2], allowing one to use rather large energy step intervals for measuring peak areas. Some operators use small energy step intervals, so the “peaks look the right shape” and feel that if the peaks look distorted, the peak areas will be quite incorrect. Nothing could be further from the truth,

and all one has to do is take some data in such instruments with different step intervals to see the effects.

Au 4f spectra taken in an instrument with approximately 100 channels of detection and a pass energy of 160 eV are shown in Fig. 2. Five energy step intervals were used, namely, 2.0 (bottom spectrum), 1.5, 1.0, 0.5, and 0.25 (top spectrum) eV. Area measurements on these five spectra are all within 2% of the average value obtained for the area. The spectrum at the top took eight times longer to acquire than the bottom spectrum, and even though the peak shape looks nice, it does not improve the accuracy of the area measurement. In such an instrument, it is generally not necessary to take

survey scan data with step intervals of 0.5 or 1 eV for peak area measurements. Minimizing analysis time is important, where possible, as commercial analytical laboratories typically charge hundreds of US\$ per hour of analysis time. Of course, where peak overlap problems might occur, a separate analysis over a small energy range with more data points per eV, or a better energy resolution, might be necessary.

Fig. 3 shows similar spectra to Fig. 2 except that the pass energy was reduced to 20 eV and an additional energy step of 0.125 eV was included in the data set. With a lower pass energy of 20 eV, the energy spread

Table 1. Peak area measurements for the Au 4f doublet taken from the spectra displayed in Figs. 2 and 3 for pass energies (PE) of 160 and 20 eV. Peak areas obtained for pass energies of 80 and 40 eV are also included in the table.

| Energy Step (eV) | Peak Area for 160 eV PE | Peak Area for 80 eV PE | Peak Area for 40 eV PE | Peak Area for 20 eV PE |
|------------------|-------------------------|------------------------|------------------------|------------------------|
| 2.0              | 229 k                   | 232 k                  | 216 k                  | 212 k                  |
| 1.5              | 229 k                   | 241 k                  | 222 k                  | 219 k                  |
| 1.0              | 229 k                   | 237 k                  | 222 k                  | 218 k                  |
| 0.5              | 225 k                   | 235 k                  | 222 k                  | 216 k                  |
| 0.25             | 223 k                   | 232 k                  | 220 k                  | 216 k                  |
| 0.125            |                         |                        |                        | 216 k                  |

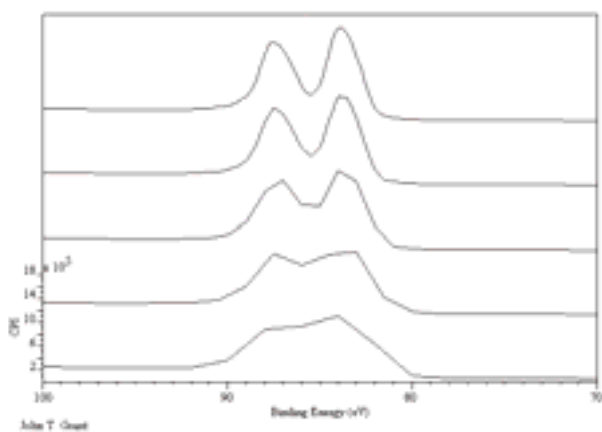


Fig. 2. Au 4f doublet taken with a monochromatic Al x-ray source in a Kratos Ultra XPS with approximately 100 channels of detection, using a pass energy of 160 eV. The energy step intervals were (bottom to top) 2.0, 1.5, 1.0, 0.5, and 0.25 eV. The spectra have been offset for clarity.

of the analyzer output across the 100 channels of detection is proportionally smaller and is now about 2 eV, so this would be the smallest pass energy where 2 eV steps would give an accurate area measurement. Of course, in practice one would never be using a 2 eV step interval at 20 eV pass energy as such a pass energy would be used

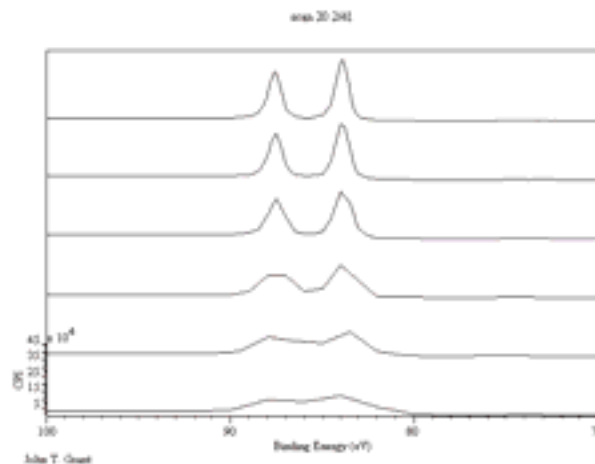


Fig. 3. Au 4f doublet taken with a monochromatic Al x-ray source in a Kratos Ultra XPS with approximately 100 channels of detection, using a pass energy of 20 eV. The energy step intervals were (bottom to top) 2.0, 1.5, 1.0, 0.5, 0.25, and 0.125 eV. The spectra have been offset for clarity.

for lineshape analysis and would require many more channels per eV. However, there are still sufficient detection channels to accurately measure peak areas with large energy step intervals, and again the peak areas are all within 2% of the average peak area.

The peak areas measured from the data shown in Figs.

2 and 3 are listed in Table 1, showing their close agreement. Note that the peak area measurements were automatically corrected for step interval and for the different analyzer transmissions at the two pass energies shown. The analyzer transmission is saved with the spectral data and used in the data processing software for measuring peak areas [3]. The peak areas calculated for the 20 eV pass energy are consistently a few percent below those calculated for a pass energy of 160 eV, indicating that the transmission correction provided by the instrument calibration procedure was not perfect.

### 2.3 Pass energies and energy step intervals in a HSA: collecting appropriate data in minimum time

Recently I was asked to help on a semiconductor project because the instrument that had been used for this project (at another university) was not available at the time. I offered to help, and was given part of an earlier report on an analysis. The instrument that I used for the analysis was similar (PHI 5700), but I noticed that the other university took two hours to acquire their survey spectra. This is much longer than the accepted norm. I also noticed that the pass energy used for the survey scan was 58.7 eV, lower than what I use (188 eV).

The energy step interval was not printed in the header with the spectra, but an attached text report stated that a step size of 1 eV was used for a survey scan and a step size of 0.2 eV was used for multiplex data (over the elements of interest). However, the pass energy used was the same (58.7 eV) for both acquisitions!

The survey scan from the other university is shown in Fig. 4. Note the acquisition time of 125 min. The text report provided (from a different sample) is shown in Table 2. I requested the raw data file from the other university to see what step interval was used for the survey scan and it was 0.4 eV, which did not agree with either of the step intervals given in the associated table. Further, the concentration table (shown in Table 2), lists values for peak heights and not peak areas, so it was not clear if the quantitative analysis was made using the peak heights listed, or actual peak areas. Such discrepancies in reports can be of great concern for the experienced user, but are often overlooked by less experienced personnel requesting an analysis

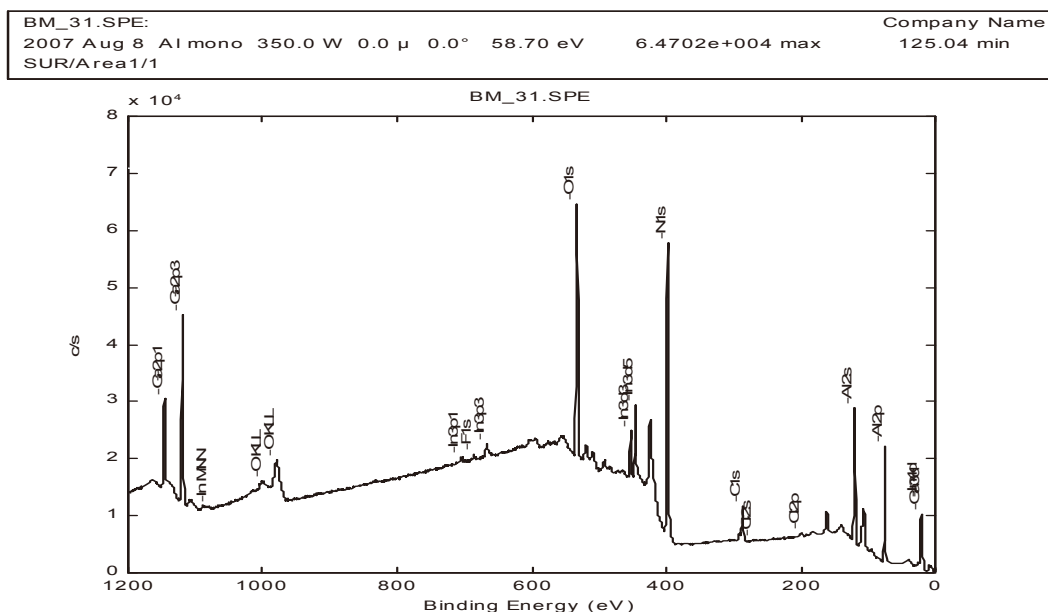


Fig. 4. XPS survey scan taken from a semiconductor sample with a pass energy of 58.7 eV, a step interval of 0.4 eV, and a total acquisition time of 125 min.

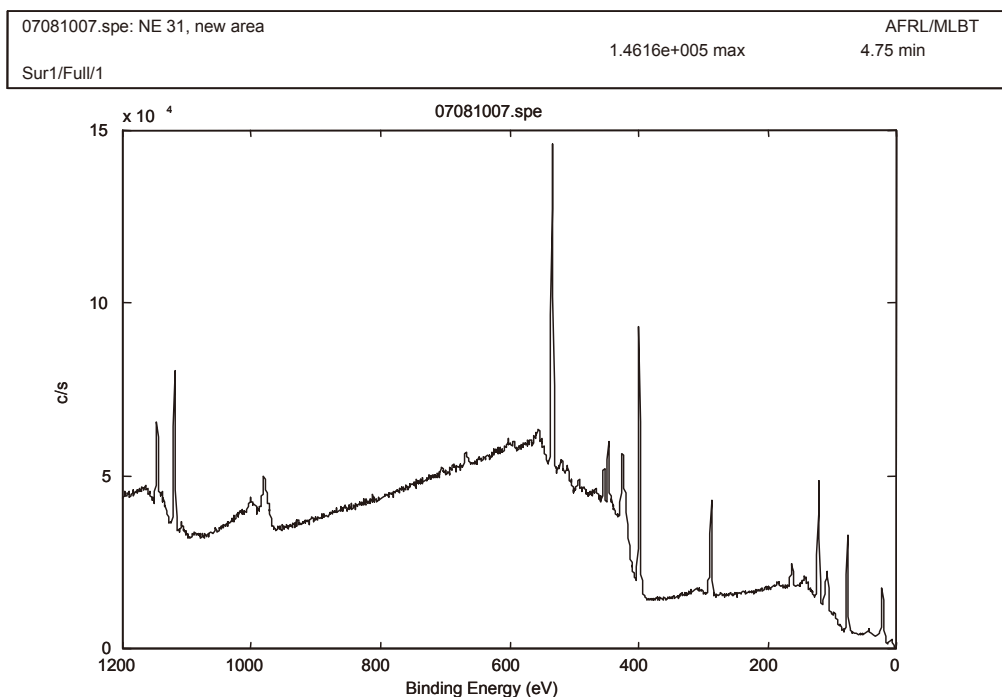


Fig. 5. XPS survey scan taken from a semiconductor sample with a pass energy of 188 eV, a step interval of 0.8 eV, and a total acquisition time of 5 min.

Table 2. Data given in a report related to the spectrum shown in Fig. 4.

AlGaIn/GaN/SiC (post reactor clean) NE31 XPS on 8-8-07.

Survey of binding energy from 0-1400eV. (DM\_960).

Pass energy = 58.7

Step size = 1eV

Area of scan = 0.8mm

Multiplex of NE01 (DM\_961)

Pass energy = 58.7

Step size = 0.2 eV

Scan area = 0.8mm

| material | Atomic orbital | Sensitivity factor | Peak position | Peak height | Atomic % |
|----------|----------------|--------------------|---------------|-------------|----------|
| N2       | 1s             | .499               |               | 110220      | 49.7     |
| Al       | 2p             | .256               |               | 82420       | 37.2     |
| In       | 3d5            | 4.530              |               | 6247        | 2.8      |
| Ga       | 3d             | .438               |               | 22830       | 10.3     |

A survey spectrum that I took from a similar sample is shown in Fig. 5. This spectrum took only 5 min to acquire (a factor of 25 times faster) and is of similar quality as that shown in Fig. 4. This spectrum was taken with a

pass energy of 188 eV and a step interval of 0.8 eV. Data at 188 eV pass energy could have been taken at a step interval of 1.6 eV for area measurements as this instrument has a 16 channel detector, and that would have resulted in a further reduction in time. This is more typical of survey spectra acquisition times needed in modern instruments.

**2.4 Acquisition times for appropriate signal-to-noise and detection limits**

A scientist was studying an adhesive bond failure (involving a Cr-based primer) and was concerned that the failure might have occurred at the primer interface. He had been looking for Cr in the XPS spectrum, and as I walked past him, he asked “do you see anything else in the spectrum besides O, Mg, C and Si? ; there isn’t any Cr.” In looking at the spectrum, the signal-to-noise was quite poor so I asked what the detection limit for Cr was in the spectrum and he just said “there wasn’t any”. He was not interested in taking any more data, since he was sure that the failure was not at the primer interface, as he did not detect any Cr.

The spectrum he took is shown in Fig. 6. From this spectrum, I later calculated the Cr detection limit to be 0.5 at.% based on the noise level in the Cr 2p region of the spectrum. Based on my experience, Cr levels detected

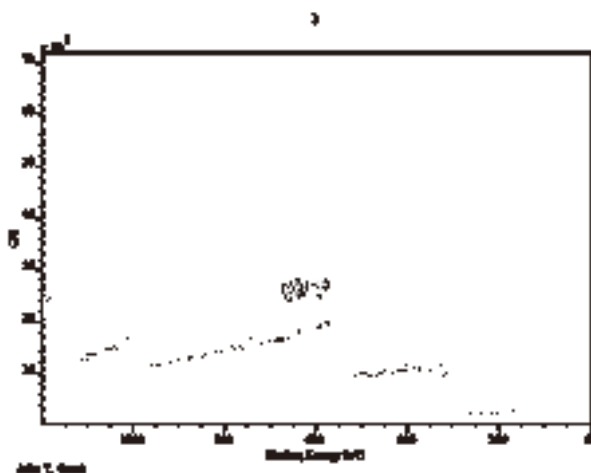


Fig. 6. XPS survey scan taken from a sample in an adhesive failure study involving a Cr-based primer. The detection limit for Cr is only 0.5 at.%.

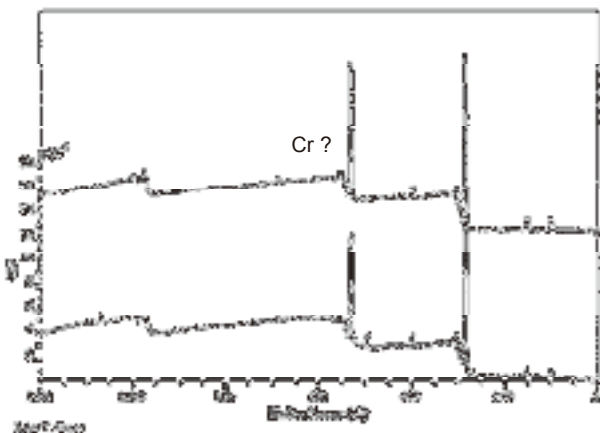


Fig. 7. XPS survey scans taken from opposite faces of an adhesive failure. The detection limit for Cr is  $\ll 0.1$  at.%. The spectra are offset for clarity.

at surfaces of Cr-based primers are often less than 0.5 at.%.

I have also studied such adhesive failures, and I feel that it is also necessary to look at both surfaces in a failure. XPS data that I had taken from two such surfaces are shown in Fig. 7. This study also involved a Cr-based primer. The most obvious difference between the spectrum in Fig. 6 and the two spectra shown in Fig. 7 is the higher signal-to-noise for the data in Fig. 7. To the casual observer, it might appear that there is no Cr peak detected from either surface in this case also. However, there is a significant difference between the spectra in the Cr 2p region of 570-590 eV, just beyond the loss structure from the O peak near 530 eV. This can be seen more

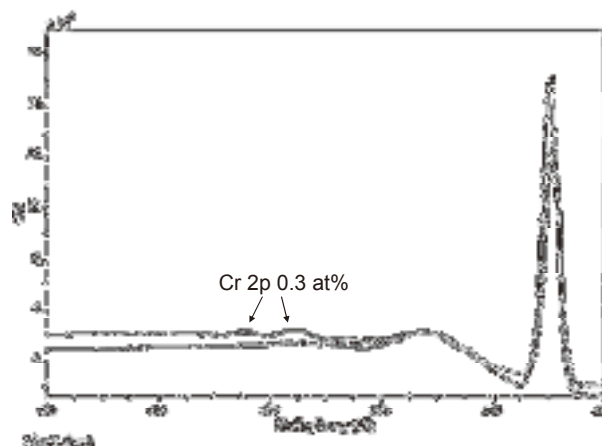


Fig. 8. XPS data from 520-620 eV binding energy showing the Cr 2p doublet detected from one side of the failure, indicating that the failure occurred at the primer interface. The main peak is O 1s.

clearly in Fig.8, where spectra from the two failed surfaces show that one surface has 0.3 at.% Cr and the other would be  $\ll 0.1$  at.%, indicating that failure occurred at the primer interface.

Acquisition times are very important as they must be sufficiently long to achieve the desired signal-to-noise for the required detection limit. It is not necessary to scan the entire survey region (typically 0-1000 eV) to get the required signal-to-noise for a certain element. It is more time efficient to scan only the energy region of interest for that element for the necessary time.

## 2.5 Possible analyzer problem involving analyzer scattering

Another interesting example concerned an instrument that was awaiting repair under a service contract with the manufacturer. I had wanted to use the instrument, but was told by the responsible scientist (who had over 20 years of experience with such equipment), that I could not use it as it was not working properly and that the service engineer had been called to repair it. I enquired as to the problem, and was told that there was a high background in part of the spectrum. The lower part of Fig. 9 shows a spectrum similar to the one that I was shown, and was told, "the background was too high in the middle and was actually sloping upwards (to the left of some peaks)". I said that it probably was not a problem with the instrument at all, and that the increasing background indicated a layered structure as has been discussed many times by Tougaard [4]. I suggested

looking at a different sample, and it turned out that there was no unusual background with it. The scientist quickly called the company to cancel the service call, and I was allowed to use the instrument.

## 2.6 Identification of peaks in spectra

An interesting situation arises in identifying the weaker peaks in the lower spectrum of Fig. 7, specifically in the region 0-300 eV binding energy. The Si peaks near 100 and 150 eV are rather obvious, as are the Cl peaks near 200 and 270 eV. The peak near 130 eV might be thought to be the 2p peak of P, but it cannot be P as the 2s peak of P is absent in the spectrum. This can be seen clearly in Fig. 10(a) where the P 2s peak (which would be near 190 eV) is absent. Careful examination of the Cl peak intensities shows that the Cl 2s peak near 270 eV is also too intense relative to the Cl 2p peak near 200 eV. Therefore a peak from some other element is overlapping

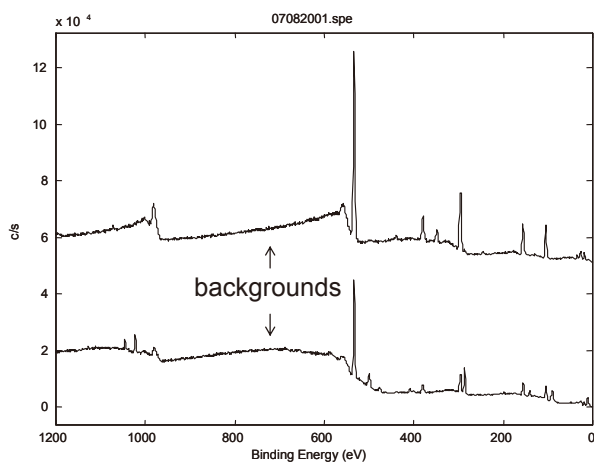
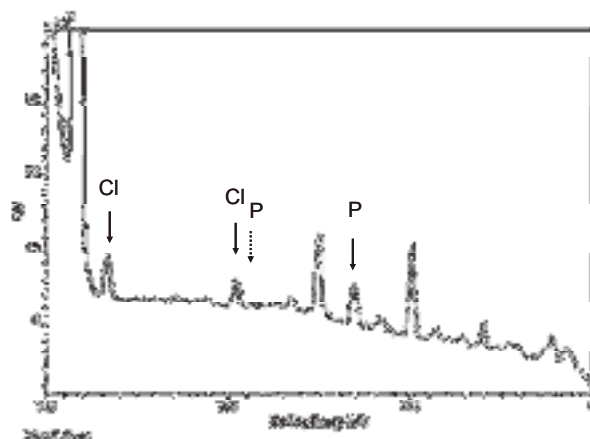


Fig. 9. XPS survey scans taken from a “defective” instrument (lower spectrum) since it had an increasing background near the center of the spectrum. A spectrum taken from a different sample (upper spectrum) did not show such a background, indicating there was no problem with the instrument. The spectra are offset for clarity.

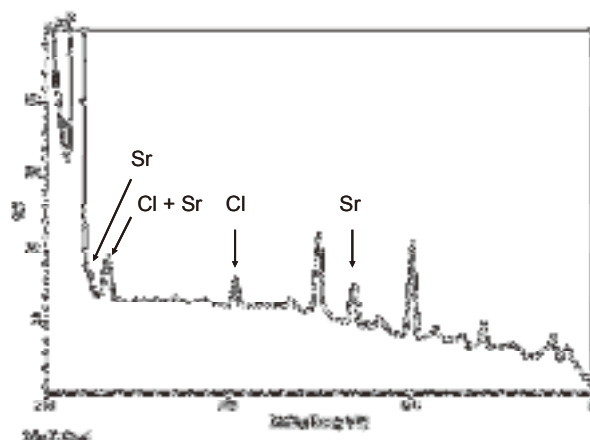
the Cl 2s peak. This other element is Sr, with its 3d peak near 130 eV. The overlapping peak near 270 eV is from Sr  $3p_{3/2}$  and the Sr  $3p_{1/2}$  peak can be seen as a shoulder on the rapidly rising C 1s peak; see Fig. 10(b). Sr could be further confirmed by taking a higher energy resolution scan of the Sr 3d region showing that this peak is a doublet with the appropriate energy separation. This is shown in Fig. 11.

It is important to check relative peak intensities before

completing a qualitative analysis. Some data processing software packages claim to do this, but I find that this is often not the case. Another example of not checking relative peak intensities can be seen in Fig. 4, where the software identified the peak near 400 eV as N 1s and neglected the fact that some of this intensity is from an Auger peak from Ga, even though Ga was identified by the software to be present in this sample.



(a)



(b)

Fig. 10. Binding energy range of 0-300 eV from Fig. 7, showing (a) the initial labeling of peaks as Cl and P (the Si peaks near 100 and 150 eV are not labeled), and (b) the final labeling of the peaks as Cl and Sr.

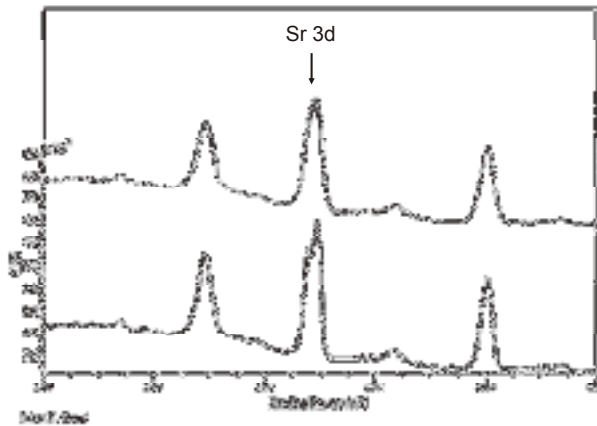


Fig. 11. The Sr 3d region of Fig. 10 (upper spectrum) taken at a higher energy resolution (lower spectrum) to observe the Sr 3d doublet and confirm the identification of Sr.

### 3. Summary

The examples shown in this paper illustrate some basic issues that can occur in the acquisition and analysis of XPS data. Care should be taken in acquiring data to minimize acquisition times for the required analysis, and also in processing data to obtain accurate and meaningful results.

### 4. References

- [1] P.W. Palmberg, J. Electron Spectrosc. Relat. Phenom. 5, 691 (1974).
- [2] I.W. Drummond, "XPS: Instrumentation and Performance", in Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, ed. by D. Briggs and J.T. Grant, Chapt. 5, pp. 117-144, IM Publications and SurfaceSpectra (2003).
- [3] CasaXPS, by Casa Software Ltd, Bay House, 5 Grosvenor Terrace, Teignmouth, TQ14 8NE, United Kingdom.
- [4] S. Tougaard, "Quantification of Nano-structures by Electron Spectroscopy", in Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, ed. by D. Briggs and J.T. Grant, Chapt. 12, pp. 295-343, IM Publications and SurfaceSpectra (2003).