The Role of the Background in Auger Electron Spectroscopy

H. E. Bishop
Atomic Energy Research Establishment

Utah State University
MERRILL-CAZIER LIBRARY

THE ROLE OF THE BACKGROUND IN AUGER ELECTRON SPECTROSCOPY

H.E. Bishop

Materials Development Division, Atomic Energy Research Establishment
Harwell, Didcot, Oxon, UK
Telephone: 0235-24141, Ext. 4487

ABSTRACT

In Auger Electron Spectroscopy (AES) the characteristic Auger peaks are superimposed on a relatively high continuum of back-scattered electrons. In the commonly used differential mode of recording Auger spectra, the influence of the background appears through its contribution to the noise and the enhancement of the Auger signal that makes a back-scattering correction necessary in quantitative AES. With the increased use of low incident beam currents to achieve high spatial resolution, the direct spectrum is increasingly used, so that a better understanding of the background is desirable. In this paper the variations of the background with atomic number, incident beam energy and angle of beam incidence are reviewed and some new experimental measurements are presented to augment existing data. The relative contributions of back-scattered primary electrons, secondary electrons and inelastically scattered Auger electrons to the background are discussed. Measurements were also made on the variation of the Auger peak height to background ratio with beam energy from which it is possible to comment on the optimum incident beam voltage for AES. Various approaches to extracting quantitative information from the peaks in the direct spectrum are discussed and a new approach to quantitative analysis based on the ratio of the magnitude of the Auger peak to a background measured in the region of 2 keV is proposed.

INTRODUCTION

Electron excited Auger Electron Spectroscopy (AES) differs from many related analytical techniques in the high background of back-scattered and secondary electrons on which the characteristic Auger peaks are superimposed. This high background has a number of practical consequences which have strongly influenced both the development and practice of the technique. In the early days of AES it was found that, because the peaks were in general much smaller than the background, it was experimentally much more convenient to display the spectrum in the differential mode and that the differential spectrum was more readily interpretable than the direct spectrum. Indeed most systems still operate in this differential mode although the direct mode has begun to find more favour recently in some applications. The ionization of surface atoms leading to Auger emission can be induced either by the primary incident beam or by the back-scattered electrons passing back through the surface. The back-scattered contribution to the Auger signal produces two effects. It leads to a matrix dependence of the efficiency of Auger production for which a correction must be made in quantitative work, and also to degradation of spatial resolution when a very fine electron probe is used. Finally the noise in the background determines the ultimate sensitivity of the technique so that it is important to know what experimental conditions should be used to achieve the best results.

In the widely used differential mode the influence of the background appears both through the matrix correction and through the contribution to the noise in the spectrum. A considerable body of work exists on the back-scattering correction but there is very little on the noise contribution. It has been found empirically that a higher sensitivity is obtained, particularly for higher energy Auger peaks, by using higher incident beam energies, and most commercial systems now offer 10 keV or more in place of the 2 to 5 keV available on earlier instruments. However, there has been little discussion as to what is actually the optimum incident beam voltage for AES, probably because it is difficult to make accurate measurements of noise.

As the technique of AES has developed attention has moved back toward the direct spectrum for a number of reasons, viz.

(1) Some elements show large chemical shifts which complicate quantitative measures in the differential mode,

but the overall peak area is not changed by the chemical state of the element involved.

(2) In Auger mapping it is much easier in the direct spectrum to correct for the effects of specimen topography, (Janssen et al, 1977).

(3) When the noise in the direct spectrum is comparable to the peak height many of the practical advantages of differentiation disappear as the overall visibility of the peak is better in the direct mode.

(4) At the low beam currents necessary to achieve high spatial resolution the signal from the electron spectrometer drops to a level where direct counting can be used. In this condition the direct mode becomes experimentally the easiest approach to adopt.

The literature on the direct mode is mainly concerned with the measurement of peak areas and the variation of peak height to background with specimen geometry. Rather surprisingly there are few if any quantitative data on how the background varies with beam energy or atomic number. The former is important in determining the peak height to noise ratio in the spectrum whilst the latter could be of significance in quantitative analysis. As Auger imaging becomes more widespread a general understanding of peak height to background ratios and of the absolute measured current in the spectrometer (and hence the noise in the signal) would be valuable both in optimising the design and the efficient use of Auger imaging. Another use of absolute measurements would be to compare different experimental systems. The most popular system is the coaxial cylindrical analyzer with a concentric electron gun. For a variety of reasons, cylindrical analysers with non-concentric guns, and also hemispherical analysers, are often used. Absolute measurements of peak heights and backgrounds for different types of specimens would greatly simplify a comparison of the relative merits of these different systems.

Our interest in the background in AES was stimulated recently when we acquired a high resolution Auger microscope (the Vacuum Generators MA 500) in our Laboratory and started to record spectra regularly in the direct counting mode. As this instrument operates at up to 30 keV we were faced with the question "What is the optimum beam voltage to use in AES?" In addition we could no longer use the spectra published in handbooks to give us quantitative information and were therefore faced with the problem of how to extract quantitative data from the spectra.

AES has now become a well established analytical technique. The period of rapid instrumental development is probably coming to an end. Over the next decade the major advances will be in data processing with increased use of computers in both data collection and processing. It is therefore a good time to assess our current procedures and speculate on how these may be improved in the future. The object of this paper is to look at those practical aspects of AES that are influenced by the background, with the exception of the back-scattering correction that is very extensively covered elsewhere (see eg. Ichimura and Shimizu 1981). In the following sections, we will first review the origin of the background and present some new measurements to augment existing data. We will then discuss what is the optimum incident beam voltage for AES and review the various ways of extracting quantitative data from the peaks in the direct spectrum.

Finally, we will consider to what extent the background itself may give useful information in quantitative analyses.

EXPERIMENTAL MEASUREMENTS OF THE BACKGROUND

In the literature we could find no detailed quantitative data on how the background varies with beam energy and atomic number. A comprehensive study covering a wide range of atomic numbers, beam angles and energies is clearly a massive undertaking and was not possible with the resources available. Instead we have aimed to produce sets of data intended to answer two specific problems of practical interest in AES. These are, what is the optimum beam voltage for AES and how does the background over the range 100-2000 eV vary with atomic number? For the former we have made measurements of the Auger peak and background intensities over a range of energies for two elements Cu and Ta which have between them peaks covering the whole range of energies used in AES. The results of these measurements have been published (Bishop, 1981). The variation with atomic number was explored by recording the spectrum from a number of elements across the periodic table of a beam energy of 10 keV.

The measurements were made in the VG Scientific MA 500. This instrument is an ultra high vacuum (UHV) scanning microscope with a three lens magnetic column, fitted with a hemispherical electron spectrometer with an input lens that allows better access to the specimen. Specimens were mounted on a stub which incorporated a small Faraday cup. (It is most important to measure beam currents carefully in a Faraday cup rather than to use specimen currents if accurate comparisons are to be made between elements and between different instruments). After cleaning by ion bombardment the specimens were tilted to an angle of 45° to the incident beam, at which angle the axis of the analyser lens is at 15° to the specimen normal. This angle has been found the most convenient for routine use in the instrument. The greatest uncertainty in these measurements was the setting of the incident angle as the specimen manipulator was not designed for accurate angular positioning, and the samples were not all accurately coplanar with the stub surface. The uncertainty in angular position was probably ±5°. This error was not important in the measurements in which the beam voltage was varied, since the same angular setting was used throughout, but significant errors may have been introduced in the measurements on different samples. A series of measurements on the variation of background with specimen angle were made to check the magnitude of this uncertainty. In all cases a beam current of 10 nA was used.

The results for the peak to background measurements are given in Table 1. The count rates are all normalised to 1 sec counting times and 10 nA beam current. In most cases the peak height was taken as the difference between the counts measured at the peak position and that measured on the high energy side of the peak, the parameter used for Auger imaging. However, for low beam energies and for the 60 eV copper peak, where there is a large background slope, the value for the background was interpolated. Table 1 demonstrates the effect of varying beam energy using a fixed analyzer retard ratio, corresponding to a nominal resolution of 0.5% similar to that used in most AES work, and Table 2 shows

Table 1

Variation of Auger peak height and background with incident beam energy

Beam Energy keV	Cu		Ta	
	57 eV	912 eV	164 eV	1670 eV
Peak heights (c/s)				
2	7500	3150	7500	—
5	5050	7500	5400	1950
10	3000	6100	3950	5150
20	1600	4150	2400	3800
30	1300	3350	1350	3500
Corresponding background (c/s)				
2	60000	93000	46500	—
5	31500	24000	29000	60000
10	18000	10500	18500	23500
20	10200	5200	10500	11300
30	7700	3550	8000	8000
Peak background				
2	.125	.03	.16	—
5	.16	.32	.19	.03
10	.17	.58	.21	.22
20	.16	.80	.23	.34
30	.16	.93	.23	.44
Peak/(background)$^{1/2}$				
2	31	10	35	—
5	28	49	32	7.9
10	22	59	29	33
20	16	57	24	36
30	15	56	21	39

Table 2

Variation of Auger peak height and background with spectrometer resolution

Retard ratio	Nominal Resolution %	Cu 912 eV (10 keV)	Ta 164 eV
Peak heights (c/s)			
1	2.0	23000	24000
2	1.0	14500	10500
4	0.5	6100	3950
10	0.2	1750	850
20	0.1	650	—
Corresponding background (c/s)			
1	2.0	67000	130000
2	1.0	31000	57000
4	0.5	10700	18500
10	0.2	2150	3500
20	0.1	630	—
Peak background			
1	2.0	.34	.18
2	1.0	.47	.18
4	0.5	.60	.21
10	0.2	.82	.24
20	0.1	1.02	—
Peak/(background)$^{1/2}$			
1	2.0	89	66
2	1.0	82	44
4	0.5	59	.29
10	0.2	38	14
20	0.1	26	—

the effect of varying the spectrometer resolution. Fig. 1 shows the spectra recorded at 10 keV under identical conditions for a selection of the elements studied. The significance of these measurements is discussed in the following sections. Fig. 2 shows the variation of the background with angle of incidence at a fixed energy, and from this can be seen that a variation of ±5° in angular setting about 45° represents a ±7% change in the background. There is therefore a possible systematic error between the different elements in Fig. 1 of up to 14% corresponding to the uncertainty in the angular position of the specimen. Fig. 3 shows the variation of the background with atomic number at certain fixed energies for all the elements studied.

ANGULAR VARIATION OF AUGER PEAK HEIGHT TO BACKGROUND RATIOS

The intensity of Auger emission is expected to show approximately a Cosec dependence on the incident angle of the electron beam, and the background also increases as the incident angle is decreased. In conventional AES where the ratio of peak heights from the elements in the differential spectrum is used to produce a quantitative analysis, the incident angle is only of interest if a back-scattering correction is applied to obtain a more precise analysis. However, if one wants to compare the distribution of a given element over a surface the topography of the surface can easily mask any effect due to changes in the effective incident angle of the beam. Fortunately Janssen et al (1977) have found that the dependence of the background intensity on incident angle is very similar to that of the Auger peaks and they were able to show how the effects of topography could be largely suppressed by recording the peak height (in either the direct or the differential mode) to background ratio. Figs. 4 to 6 show the results of a set of measurements taken in our laboratory to check this result for one of our own instruments.

Fig. 4 shows the E.N(E) spectrum obtained from a contaminated iron specimen as it was rotated. The spectrometer was of the half-cylinder CMA (cylindrical mirror analyzer) type with a phosphor-photomultiplier detector rather than the conventional electron multiplier so that both the direct and differential spectra were available. Both the overall shape of the background and the Auger peak heights were found to behave as predicted.
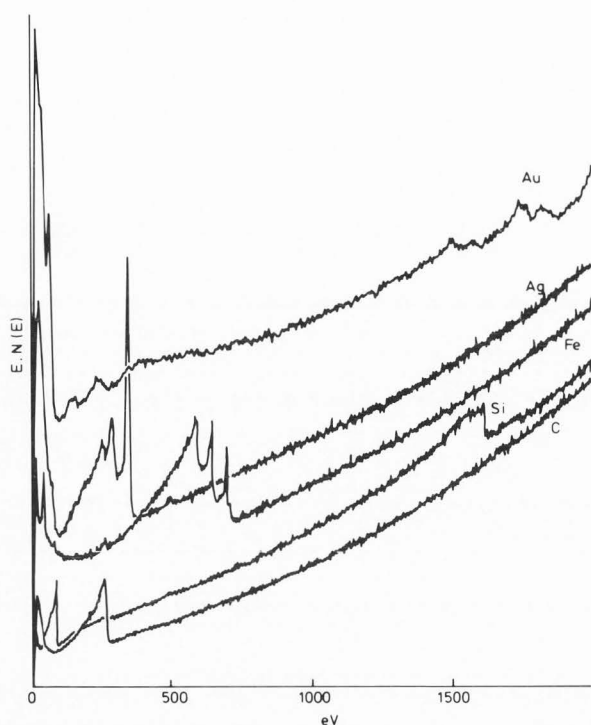
Fig. 1   E.N(E) spectra for a range of elements recorded with a 10 nA beam at 10 keV, and 45° incidence, plotted with the same zero and sensitivity.
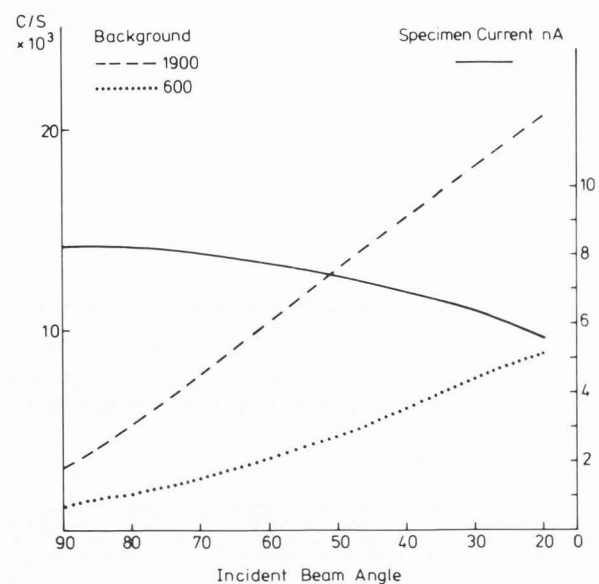

Fig. 2   Variation of background and specimen current with incident beam angle for Si.
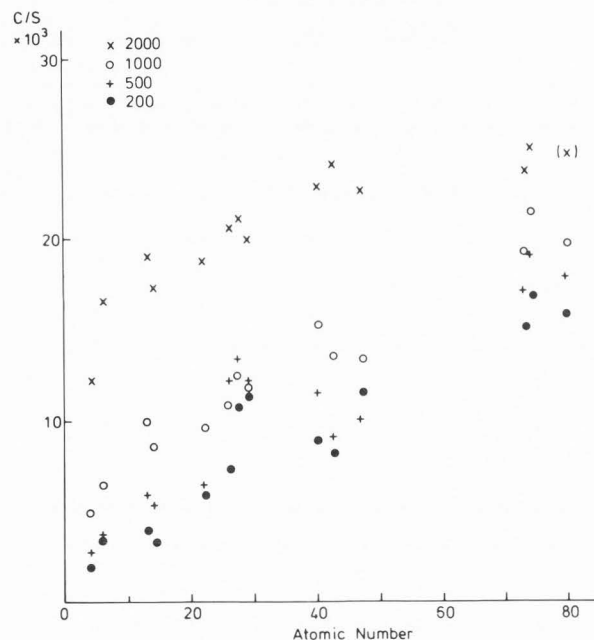

Fig. 3   Variation of background with atomic number with the same conditions as in Fig. 1. Value for gold interpolated to remove contribution from Auger peak.

Curve 1 in Fig. 5 shows how the background at 710 eV varies with specimen angle. Curves 2 and 3 are the ratios of the backgrounds at 510 eV and 290 eV to background at 710 eV. These two ratios are almost independent of angle, thus, although the absolute value of the background varies by a factor of 4 over the range of angles investigated, the overall shape of the background hardly changes as the specimen is rotated. The variation of the Fe L_3VV peak to peak height with angle is shown in Fig. 6 together with the ratio of p/p height in the differential spectrum to background in the direct spectrum. A similar behaviour was found for the O and C peaks. Again the variation with angle is largely suppressed in the ratio. The rise in the ratio as one approaches glancing incidence was also observed by Janssen et al (1977). On clean Cd and Zn the effect was much more marked than in Fig. 6 but the variation for O and C on uncleaned Zn were quite comparable to our results.

The insensitivity to the incident beam angle of the overall shape of the electron spectrum over the energy range used in AES, demonstrated by Janssen et al (1977), is of great practical importance. They have shown that the technique of taking ratios can effectively eliminate the effects of topography. In addition the constant shape means that the shape of the spectrum needs be investigated in detail for only one incident angle to gain an overall view of the behaviour of the spectrum over a wide range of angles, bearing in mind that there may be significant variations at the extremes of grazing incidence or take-off angle.

THE ORIGIN OF THE BACKGROUND

When an electron beam strikes a solid the energy spectrum of electrons leaving the specimen has conventionally been divided into three components: the elastically scattered component, the low energy peak of secondary electrons (rather arbitrarily defined as those electrons leaving the specimen
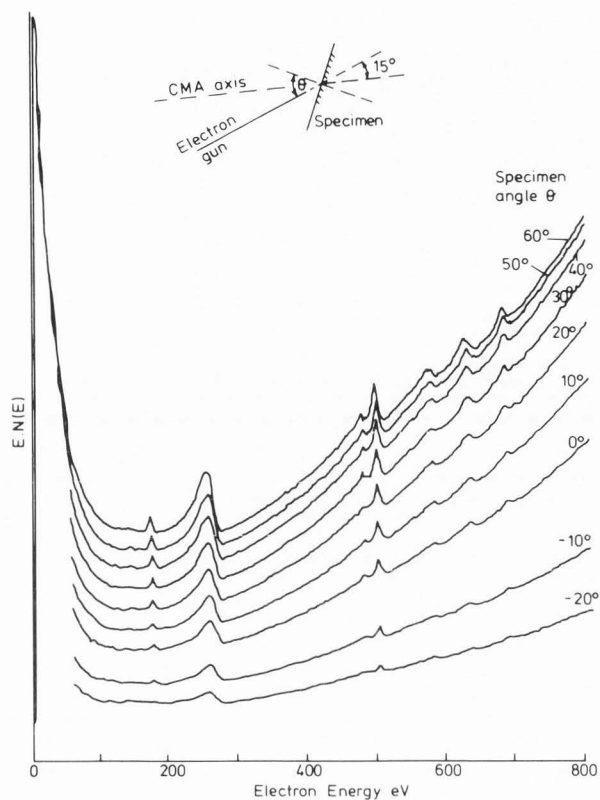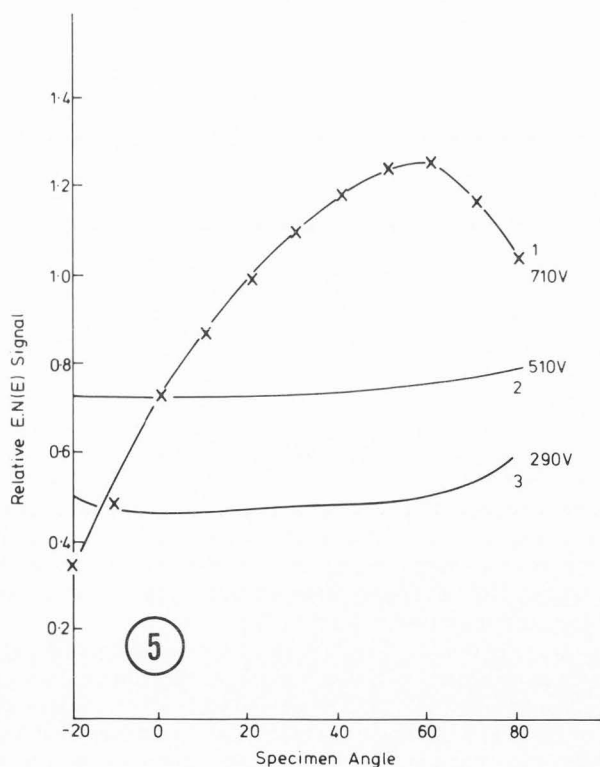
Fig. 4   **Variation of E.N(E) with specimen angle, incident beam energy 2.5 keV.**

with less than 50 eV energy), and a broad spectrum of inelastically scattered primary electrons. The arbitrary division between back-scattered and secondary electrons is made purely for experimental convenience when measuring electron back-scattering. In recent years the main motive for the measurements of the overall energy spectrum of back-scattered electrons has been the determination of the back-scattering correction in electron probe X-ray microanalysis (Bishop 1965, Darlington 1975) and more recently of the equivalent correction in AES. These measurements have been made at relatively low resolution and have not covered the background in the 100-2000 eV region in sufficient detail to be of assistance for our present purposes. Since we wish to determine the relationship between the background and Auger peak intensities we have had to augment the measurements in the way described above. There is however sufficient information available to understand the main mechanism producing the background and to give an overall view of how the background behaves.

The dominant features of electron back-scattering may be understood by considering the fraction of incident electrons that are back-scattered, η, and the overall energy spectrum of these electrons. Typical values for η and for the energy spectrum are given in Table 3 and Fig. 7 (Bishop, 1965). Table 3
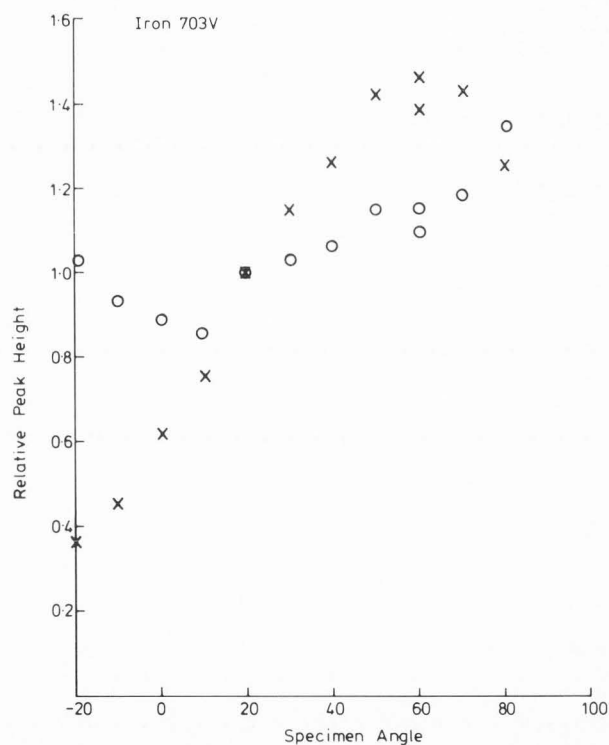

Fig. 6   **Variation in magnitude of Fe Auger signal with specimen angle. X differential peak to peak signal normalised to unity at 20° 0 peak to peak signal divided by background at 710 eV.**

Fig. 5   **Variation of background at 710 eV with specimen angle (1) and ratio of backgrounds at 510 eV (2) and 290 eV (3) to background at 710 eV.**

Table 3

Backscattering Coefficient of Elements ($\times$ 100)

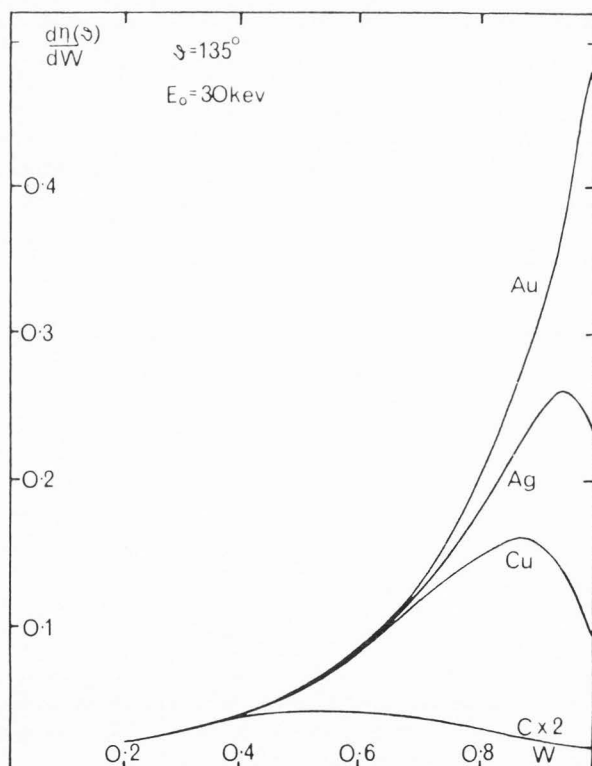|	Z	E_0		
		30	10	5
Carbon	6	6.0	7.2	8.5
Aluminum	13	15.5	17.7	18.6
Silicon	14	16.2	18.6	19.7
Titanium	22	25.4	26.8	27.0
Chromium	24	27.0	28.3	28.5
Iron	26	28.8	29.6	30.0
Nickel	28	30.8	32.3	33.3
Copper	29	31.9	33.9	35.2
Zinc	30	33.0	34.2	35.2
Germanium	32	33.4	34.9	36.2
Molybdenum	42	38.5	38.1	36.7
Silver	47	42.0	42.0	41.8
Tungsten	74	50.1	48.3	47.2
Platinum	78	51.6	50.3	48.6
Gold	79	52.1	50.1	48.9
Uranium	92	53.4	51.3	49.5

Fig. 7 **Overall energy spectrum of backscattered electrons for normal beam incidence. The energy scale is expressed as a fraction w of the incident beam energy.**

shows that the back-scattering increases with atomic number of the target material but that there is very little dependence on beam energy. Another important property of the energy spectrum is that when it is plotted with reduced energy coordinates as in Fig. 7 it is again almost independent of beam energy. One important consequence of this is that the intensity of the background in the region of the main Auger peaks will be expected to fall as the inverse of the beam energy if not more rapidly.

The variation of η with atomic number can be explained in terms of the relative importance of elastic and inelastic scattering of electrons in the target material. Angular scattering is produced by the elastic Coulomb scattering of electrons by the atomic nucleus while energy loss is through electron-electron interactions. Elastic scattering increases with atomic number and this increase is reflected in the observed increase in backscattering. Another consequence of the increase in large angle elastic scattering for high atomic numbers is that the electrons backscattered from a heavy element travel on average a shorter distance in the target than is the case for the lighter elements and hence lose less energy. Fig. 7 demonstrates both effects clearly. The total backscattering represented by the area under the curves increases with atomic number although the increase is mainly confined to the higher end of the spectrum. Indeed in Fig. 7 the energy spectra of Cu, Ag and Au are indistinguishable below half the primary beam energy. In Fig. 3 the background at 2 keV does show some increase with atomic number but this variation is small compared to the corresponding changes in η and in the backgrounds at lower energies.

The mechanism producing the back-scattering behavior described above is the scattering of primary electrons in the solid. All the features of back-scattering above about 2 keV can be well reproduced by Monte-Carlo calculations that consider only the scattered primary electrons (e.g. Bishop, 1967). Secondary electrons clearly do not make a major contribution to the higher energy component of back-scattered electrons but we still have to consider their effect in the 100-2000 eV range used in AES. The secondary electrons fall into three categories:

(1) Auger electrons themselves originating near the surface of the specimen.
(2) Inelastically scattered Auger electrons from the surface or from deeper within the sample.
(3) Directly produced secondaries, ejected from an atom as it is ionized by a more energetic electron (itself either a primary or a secondary).

The contributions from the first two sources are easily recognizable in the energy spectra shown in Fig. 8. Each source of electrons has associated with it an energy tail of electrons similar to that produced by an incident beam of the same energy. Thus for every Auger peak there is a consequential increase in the background at all lower energies. However in most cases, certainly for the more energetic Auger peaks, this represents a relatively small contribution to the background away from the peak itself.

Directly produced secondaries are much more difficult to recognise as they form a continuous distribution with no characteristic peak. This is an area where theoretical models of electron scattering can make a significant contribution to our understanding. An approximate theory to describe the shape of the secondary electron cascade using the Boltzmann

diffusion equation was derived by Wolff (1954) for electron energies below 100 eV. This theory predicted that above about 10 eV the observed shape of the energy distribution should obey a simple power law:

$$N(E) \propto ^{-m}$$

Sickafus (1977 a & b) in proposing his "linearised cascade" theory has shown that this power law behaviour can be usefully extended up to 1000 eV or so. If the energy spectrum is plotted on a log log scale he showed examples where the spectrum became a series of linear segments with each source of Auger electrons leading to a change in slope.

Ichimura and Shimizu (1981) and Shimizu and Ichimura (1981) have included the effects of high energy secondaries in their latest Monte-Carlo calculations aimed at calculating the back-scattering correction in AES. Their results show that these electrons make a very significant contribution to the background intensity below 2 keV, for a 10 keV primary beam energy. The contribution increases with atomic number and is the dominant component for elements heavier than Al for energies below 1 keV. The data from the Monte-Carlo calculations unfortunately suffer from very poor statistics in the region of interest and can give only a qualitative indication of the effect, but the indications are that we must expect to see a much greater atomic number dependence in the background below 1 keV than is evident at 2 keV. This expectation is confirmed by experimental spectra from Si, Cu and Au published by Ichimura et al (1980) and by Figs. 1 and 3. If one ignores the contribution from Auger peaks, the background at 2 keV shows a much smaller variation with atomic number than at, say, 500 eV. This difference is due to an increased contribution from secondary electrons at the lower energies as one would not expect the relative contribution from the back-scattered primary electron to change significantly in this energy range.

The main object of the paper by Ichimura et al was to explain a departure from the linearised cascade theory that appeared above the Si L peak. Fig. 9 shows the effect recorded on our MA 500 Auger instrument. They explained this feature in terms of the interaction of the back-scattered electrons with the silicon L shell and were able to show theoretically that a background that obeyed the power law in the absence of the silicon L edge took on the shape observed experimentally if the L edge were present. Sickafus (1977b) observed a similar feature in the spectrum of Al cleaned by ion bombardment but attributed it to emission from oxygen below the surface of the sample. A broad peak was also observed by Ichimura et al. (1980) in the clean gold spectrum. As a result of the presence of such features the attractive theory of linear cascades for background subtraction proposed by Sickafus must be treated with some caution.

THE OPTIMUM INCIDENT BEAM VOLTAGE FOR AES

The optimum conditions for any analytical technique are those that achieve the maximum signal to noise (S/N) ratio subject to any constraints set by either the instrument or the specimen. In AES one or more of the following factors may limit the sensitivity:
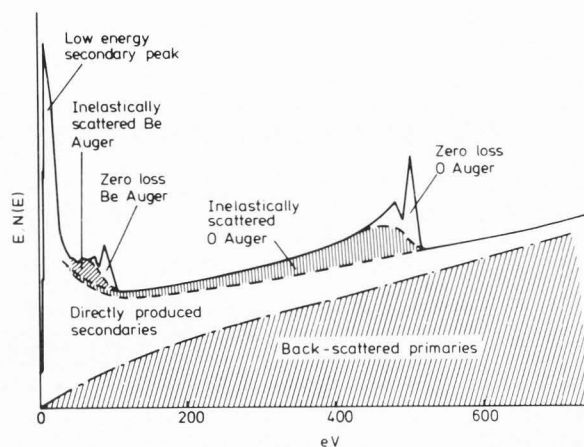

Fig. 8 E.N(E) spectrum for oxidised Be showing schematically the various contributions to the background.
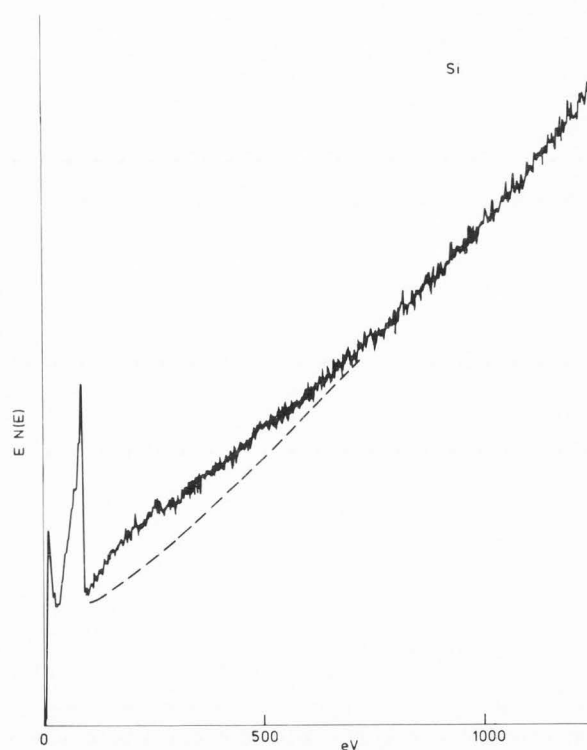

Fig. 9. E.N(E) curve for Si from Fig. 1 illustrating the departure of the background from a simple power law on the high kinetic energy side of a major Auger peak. The dashed curve shows extrapolation of high energy background expected from a simple power law.

(1) The need to achieve a high spatial resolution.
(2) The maximum temperature rise that the specimen can tolerate.
(3) The electron dose that will induce significant changes in the surface composition — either radiation damage or beam induced diffusion, adsorption or desorption.
(4) Specimen charging.

In the last case, beam energy and angle of beam incidence have to be adjusted to eliminate charging before any measurement is possible.

Before considering these points it is necessary to know how the S/N ratio varies with beam energy for a fixed current. Janssen et al (1977) have shown that the peak height to background ratio (P/B) is still improving with increasing beam energy at 60 keV, but they make no comments on the S/N ratio. Although the ionization cross-section is known sufficiently well to be able to calculate the variation of Auger yield with beam energy, there is not a corresponding theory for the variation in the background; hence the need to use experimental data. Experimental measurements of the Auger signal are straight-forward but an accurate measurement of the noise, using analogue recording, is more difficult as conditions have to be very carefully defined, particularly if comparisons are to be made between different systems. Fortunately, when electron counting techniques are used the recorded counts should ideally obey Poisson statistics where the standard deviation of the measurement is equal to the square root of the recorded count. Thus the $P/\sqrt{B}$ ratio provides a convenient measure of the S/N ratio for a given peak in a spectrum, is easily derived, and is not sensitive to the exact nature of the recording chain as is the case in measurements taken from a recorder trace. Besides providing a useful tool to identify the optimum operating conditions for a particular instrument, however, the $P/\sqrt{B}$ ratio derived under well defined conditions, together with the peak count rate, can also allow precise comparison between different instruments. An ability to make such a comparison is becoming increasingly important as more instruments using different types of analyser come onto the market. It is however important that the true beam current is recorded rather than the specimen current as the latter varies with angle of beam incidence, atomic number and to some extent with size and shape of the experimental chamber. In the measurements described in Section 2 the specimen current, measured with a 50 V bias, varied from 0.86 to 0.44 of the incident current measured in the Faraday cup, between Be and Au, respectively.

Table 1 shows P/B and $P/\sqrt{B}$ ratios derived from our measurements. As might be expected from the ionization cross-section, the peak heights pass through a maximum and then decrease with increasing energy. The P/B ratios on the other hand increase with beam energy apparently reaching a saturation value for the lower energy peaks. Janssen et al (1977) measured the P/B ratio for the Cd 380 eV Auger peak and found this to be still increasing at 60 keV, although they were using a very low incident angle (10°). The increase in P/B ratio with energy is however offset by a drop in signal at higher beam energies, as a result of which the S/N as measured by the $P/\sqrt{B}$ ratio is observed to pass through a broad maximum for the Cu 912 eV line. The maximum for the

lower energy Cu line is below 3 keV while that for the high energy Ta line is above 30 keV. The results from variation of the analyzer resolution in Table 2 show that for the peaks considered the reduction in P/B found on degrading the resolution is more than offset by the increase in signal as far as S/N is concerned. When maximum sensitivity is required, as in Auger mapping, it would appear that the lowest resolution, compatible with resolving the features of interest, should be employed in our instrument.

The information in Table 1 gives a basis for deciding the optimum beam voltage to use in AES. At first sight if no special circumstances have to be considered there seems little advantage in using a beam energy above, say, 10 keV, where the high energy lines are adequately excited and the sensitivity of the low energy lines has not started to drop off. This is however to ignore the properties of the electron optical system delivering the exciting beam. The brightness of an electron source is proportional to the beam energy which means that the current that can be delivered into a probe of given size is in turn proportional to beam energy. The $P/\sqrt{B}$ figures in Table 1 are for a fixed beam current. For a fair comparison of the AES performance at different beam energies (E) these figures should be scaled by $\sqrt{E}$ to allow for the higher current available at higher beam energies. Once this is done a clear advantage appears for using the highest available beam energy. Indeed Janssen (1977) et al favour their maximum energy, 60 keV, for high spatial resolution AES studies. On the other hand, at such high voltages the spread of the beam in the specimen is considerable and the back-scattered contribution to the AES signal will come from a relatively large area complicating the interpretation of the results.

For beam sensitive materials the choice of beam energy is more complex. If there is simply a temperature limitation the power in the beam must be limited, which may be achieved by reducing either the beam current or the voltage. Under these circumstances the advantage probably moves to lower beam energies although this will depend on the spatial resolution required.

In a case where beam induced effects must be minimised Bauer and Seiler (1980) have shown that for a given detection limit there is a minimum probe size that may be achieved depending on the sensitivity of the material to electron dose. The radiation damage in the surface layer is proportional to the energy dissipated in the layer which in turn is approximately proportional to $\sqrt{E}$. For a given surface damage rate there may therefore still be a slight advantage in using a higher beam energy.

VARIATION OF THE BACKGROUND WITH ATOMIC NUMBER

The series of spectra shown in Fig. 1 illustrate clearly that the background in general increases with atomic number. This increase is much more marked at the lower energy end than at higher energies. The relatively small variation at higher energies is in agreement with measurements of the total spectrum and with Monte-Carlo calculations. It would appear therefore that the contribution to the background from back-scattered primary electrons does not vary much

with atomic number and that the main source of the observed increase is from high energy secondary electrons.

The results in Fig. 1 are for pure elements. It is interesting to speculate how the background might behave for uniform compound materials and, for the case that is usually of interest in surface analysis, that of a thin layer of one material on another. The overall back-scattering coefficient for a compound depends on the mass concentrations of the constituent elements, and the overall energy spectrum approximates to that from an element of the same mean atomic number calculated from a weighted average based on mass concentrations (Bishop 1968). The Auger intensity on the other hand depends on the atomic concentration of the element concerned and on the escape depth. Considering the behaviour of the low energy background, the main concentration dependence of the back-scattering and also of X-ray production from the bulk of the sample is a result of the way electron stopping power depends on atomic number. Very crudely the stopping power of an element depends on the number of electrons per atom and thus its atomic number. The low energy spectrum however is dominated by the mean free path of low energy electrons and the atomic concentration of the elements. The mass concentration will enter only through the flux of high energy back-scattered electrons. Thus we might expect the dependence of the low energy background to fall between the two extremes of mass and atomic concentration but to tend more towards the latter.

From the practical point of view for quantitative AES possibly the most significant feature of Fig. 3 is the relative insensitivity to atomic number of the background in the region of 2 keV. It has already been established that the ratio of Auger peak size to its background is insensitive to topography, as is the overall shape of the background. Therefore the ratio of the magnitude of a given Auger peak to the background at say 2 keV is a measure of the Auger intensity approximately independent of both atomic number and topography. (It may be necessary to choose a different voltage to avoid a major Auger peak e.g. Au.) Thus if the ratio is known for a standard of known surface composition and for some unknown sample we should be able to calculate the concentration of the element concerned from the relative values of the two ratios, *without measuring any other peaks*. The simplest approximation would be to write

$$C_i = C_o \frac{f_i}{f_o} \qquad (1)$$

where C is the concentration and f the measured ratio with subscripts i and o representing the unknown and a standard, respectively. A more precise form would be

$$C_i = C_o \frac{f_i}{f_o} \cdot \frac{\lambda_o}{\lambda_i} \cdot \frac{r_o}{r_i} \cdot \frac{\alpha_o}{\alpha_i} \qquad (2)$$

where λ is the escape depth, r the back-scatter correction and the α terms, inversely proportional to the background at 2 keV, allow for the small variation of background with atomic

number of the substrate. As the atomic number dependence of the corrections r and α are in the opposite sense they will partly cancel each other. If such a scheme is found to work reasonably it would be particularly valuable in routine analysis where often the specimen is too inhomogeneous to justify a rigorous quantitative analysis but where an estimate of how much or how little of a given element is present is frequently required.

QUANTITATIVE AES

As AES is traditionally recorded in the differential mode the majority of experience in quantification is for this mode. Semiquantitative analyses are obtained by taking the ratio of peak heights and using sensitivity factors either obtained directly from standards or from one of the handbooks of standard spectra. Scanning images or depth profiles are produced by displaying the variation in a given peak height either as the beam is scanned over the specimen or as the specimen is eroded under ion bombardment, respectively. When data are recorded in the direct E.N(E) mode the question arises as to what is the best measure of the Auger peak intensity for a given application. It is reasonable to assume in the following discussion that the data are acquired in a computer system of some kind and that at least straightforward operations such as smoothing, peak area measurement, differentiation etc. can be performed easily. It is convenient for discussion to divide the data into three broad categories although in real life there will be a considerable overlap:

(1) Overall analysis of surface composition.
(2) Elemental mapping.
(3) Detailed analysis of Auger line shapes.

Seah (1979) has discussed whether it is preferable to use the direct or the differentiated spectrum for obtaining quantitative data and concluded that the problems in defining an accurate peak area in the direct spectrum for routine analysis had yet to be solved and recommended the use of the differential. Nevertheless there are still advantages in recording data in the direct mode and subsequently differentiating numerically. The main advantage is that in the differential mode one has to choose a modulating voltage that is a compromise between resolution and sensitivity. If the data are recorded in the direct mode they are recorded with the full resolution of the analyser and the effect of different modulation voltages can be reproduced at will by modifying the degree of smoothing in the differentiation algorithm used in the computer program. One practical point that does merit some detailed analysis is the optimum sampling frequency to be used when recording data digitally. Ideally one should record with voltage steps small compared to any features of interest; however if too many data points are recorded one runs into memory and speed problems with smaller computers.

The first step in extracting quantitative data from the direct spectrum is to remove the background. The simplest approach would be simply to measure peak heights. This approach suffers from the same problems as differentiation. In order to measure peak areas some smooth curve has to be

fitted to the background and extrapolated beneath the Auger peaks. This curve may be either continuous, fitted to all areas away from Auger peaks (Staib 1973; Hesse et al 1976) or segments fitted to the background on the high energy side of the peak to be measured (the Sickafus 1977a linearised electron cascade approach). In the case of a continuous curve the point at which the curve rejoins the background on the low energy side of a given peak is not well defined and introduces an undesirable arbitrariness into the measurements. It can also only be used in situations where the peaks are well separated. A better defined peak area can be obtained by segmented background stripping, followed by removal of the inelastic tail by algorithms similar to those used in X-ray Photoelectron Spectroscopy (Sickafus 1980). However one is still left with the problem of close or overlapping peaks.

A promising approach to the problem of overlapping peaks has recently been described by Strausser et al (1981). They were studying the Cu, Co, Ni system where the L spectra all overlap. They found that they could determine the relative abundance of these elements by stripping standard spectra after removing the backgrounds by the linearised cascade approach. A similar stripping approach is used very successfully for energy dispersive X-ray spectra (see eg. McCarthy 1980). In this case the background is suppressed by passing a "top hat" cross-correlation function through the spectra (a process analogous to differentiation) and then performing a least squares fit. It seems likely that this approach could usefully be adopted for AES although there may be difficulties in obtaining standard spectra to match some chemical shifts.

In elemental mapping the highest priority has to be placed on the efficiency of data collection if frame times are to be reduced to an acceptable level. Clearly the most efficient procedure is to sample the spectrum at two points, representing the full step height of the peak, i.e. the peak position and the minimum on the high energy side of the peak. This can be achieved either by explicitly setting the analyser voltage and recording the peak and background values or by using square wave modulation. Topographical effects can be largely eliminated by using either $(P-B)/B$ or $(P-B)/(P+B)$ as a measure of the peak height (Prutton et al 1981). Sampling times should be chosen so that the statistical noise is just tolerable. Working in the counting mode and knowing peak to background ratios it should be possible to make this choice in terms of a known detection limit for a given element.

When AES is being used for surface analysis one is normally concerned with deriving a number proportional to the surface concentration of an element (or that proportion of an element in a given chemical bonding state). In some studies one is interested in the shape of the Auger peak itself. Here more sophisticated data analysis may be justified such as self-deconvolution (see Smith and McGuire 1981 for brief review). It is probably best to approach such studies pragmatically choosing the background stripping technique that gives the most physically acceptable results. One should however always bear in mind when considering this type of work that no exact method exists for removing the background and that there is always an element of uncertainty in the results obtained.

CONCLUDING REMARKS

The background continuum of electrons has always played an important role in AES but in most cases workers have ignored its presence because it is suppressed by differentiation. With instrumental changes the direct spectrum with the background present is becoming more generally available. Although in many ways it is a nuisance, introducing unwanted noise into the measurements of the Auger peaks, it also carries information in its own right and deserves further study.

Perhaps the most important application of the background is in Auger imaging where normalization of the peak height by the background effectively suppresses the topographical effects which make simple Auger images difficult to interpret. The measurements of variation of background with atomic number reported here show that at relatively high energies in the 2-3 keV region the background varies only slowly with atomic number. This slow variation provides the prospect of using the Auger peak height to high energy background ratio as an absolute measure of the surface abundance of an element without reference to the other elements present on the surface. More work is needed to establish the limitations of this approach but it promises to provide the basis at least for a simple semi-quantitative surface analysis. More detailed analysis of Auger peaks and their inelastic tails can provide information on the chemical state and the depth distribution of elements on the surface.

REFERENCES

Bauer HE and Seiler E. (1980). The limitation of lateral resolution in scanning Auger microscopy by radiation damage. Electron Microscopy 1980 **3**, 7th European Congress on Electron Microscopy Foundation, Leiden, 1980, 214-215.

Bishop HE. (1965). Some electron backscattering measurements. Proc. 4th Int. Conf. on X-ray Optics and X-ray Microanalysis (Paris: Hermann), 153-158.

Bishop HE. (1967). Electron scattering in thick targets. Brit. J. Appl. Phys. **18**, 703-715.

Bishop HE. (1968). The absorption and atomic number correction in electron probe X-ray microanalysis. J. Phys. D. **1**, 673-684.

Bishop HE. (1981). On the optimum incident beam voltage for Auger electron spectroscopy. Inst. Phys. London, U.K. Conf. Ser. No. 61, 435-438.

Darlington EH. (1975). Backscattering of 10-100 keV electrons from thick targets. J. Phys. D. **8**, 85-93.

Hesse R, Littmark U and Staib P. (1976). A method of background determination in quantitative Auger spectroscopy. Appl. Phys. **11**, 233-239.

Ichimura S, Le Gressus C, Shimizu R, Goto K and Massignon D. (1980). Etude de fond continu associé à l'émission d'electrons Auger. C.R. Acad. Sc. Paris. **291**, B 67-70.

Ichimura S and Shimizu R. (1981). Backscattering correction for quantitative Auger Analysis. Surface Science **112**, 386-408.

Jansen AP, Harland CJ and Venables JA. (1977). A ratio technique for micro-Auger analysis. Surface Science **62**, 277-292.

McCarthy JJ. (1980). Analysis of X-ray spectra by filtered least-squares fitting. Scanning Electron Microscopy, 1980; II:259-270.

Prutton M, Peacock DC, El Gomati MM, Larson LA and Poppa H. (1981). Normalisation of Auger electron images for beam current fluctuations and sample topography. Inst. Phys. London, U.K. Conf. Ser. No 61, 443-445.

Seah MP. (1979). Quantitative Auger Electron Spectroscopy: via the energy spectrum or the differential. Surface and Interface Analysis **1**, 86-90.

Shimizu R and Ichimura S. (1981). Quantitative analysis by Auger Electron Spectroscopy, Technical Reports Toyota Foundation No. 1-006, 76-0175 (Toyota Foundation, Tokyo).

Sickafus EN. (1977a). Linearised secondary electron cascades from the surfaces of metals. **I.** Clean surfaces of homogenous specimens. Phys. Rev. B **16**, 1436-1447.

Sickafus EN. (1977b). Linearised secondary electron cascades from the surfaces of metals. **II.** Surface and subsurface sources. Phys. Rev. B **16** 1448-1458.

Sickafus EN. (1980). A secondary electron emission correction for quantitative Auger yield measurements. Surface Science **100**, 529-540.

Smith KK and McGuire GE. (1981): Signal processing techniques in Auger electron spectroscopy. Microbeam Analysis 1981. Geiss RR (ed.), San Francisco Press, 35-47.

Staib P. (1973). A depth analysis of cleaved mica surfaces monitored by Auger spectroscopy. Radiation Effect **18**, 217-219.

Strausser YE, Franklin D and Courtney P. (1981). Digital Auger data processing in Ni-Co alloy films and Cu/Ni-Co layered structures. Thin Solid Films **84**, 145-153.

Wolff PA. (1954). Theory of Secondary Electron Cascade in Metals. Phys. Rev. **95**, 56-66.

WRITTEN DISCUSSION

Questions for author:

R. Shimizu: Figure 1 suggests that the backgrounds of those spectra are of quite similar form except for that of Au. How about the possibility to represent those backgrounds by a simple function?

Author: The work of Sickafus (1977a) shows that in many cases a simple power law may be used to fit the background above the Auger peaks. However the results for Si and Au show that such an approach is not universally applicable.

R. Shimizu: Have you ever tried to apply your approach (Eq. 1 or 2) to a sample of known surface composition? Or can you propose any appropriate sample for this? How about accuracy in the quantitation in rough estimation?

Author: I have not yet been able to test these ideas systematically. Accurate quantitative surface analysis is only possible on very well defined systems where calibration is usually possible. I would hope this approach will prove at least as good as the current approach based on peak to peak heights and relative sensitivity factors.

I hope to be examining a number of compounds of known composition, fractured in vacuum where possible, to test the validity of equations 1 and 2.