

## ON THE RESTORATION OF AUGER LINE SHAPES

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A simple and efficient method to deduce the true Auger spectrum from the raw data is presented. This method is an application to Auger spectroscopy derived from signal processing procedures employed in different fields. It appears particularly promising when complex spectra are analyzed as it avoids spurious information to be introduced. The method is also compared with the more-standard van Cittert's approach. An experimental check of the common assumption that an Auger electron experiences almost the same energy-loss mechanisms as a nearly elastically reflected primary electron at the same energy is given.

### 1. Introduction and restoration procedure

Auger electron spectroscopy (AES) is a well established technique to explore solid surfaces. The main problem one encounters in using AES is the distortion of the true signal by the energy-loss phenomena affecting the escaping electrons and also, in the case of electron excitation, by the presence of an intense primary background.

It is now well established that the primary background contribution can be reasonably estimated by a lower-power polynomial of the kinetic energy or, alternatively, by a properly chosen exponential law [1,2]. However the effect of finite instrument-resolution and inelastic losses, represented by a function  $G(E, E')$ , must be carefully considered to recover the clean Auger spectrum,  $A(E)$ , from the measured (and primary-background subtracted) one,  $N(E)$ . Once  $G(E, E')$  is known, the measured and true spectra are connected through the relationship

$$N(E) = \int_{-\infty}^{+\infty} A(E') G(E, E') dE' = \int_{-\infty}^{+\infty} A(E - E') G(E, E') dE'. \quad (1)$$

In eq. (1) it has been assumed that  $G(E, E') \approx G(E - E')$ , so that the

integral equation is reduced to a convolution product. Such an approximation is expected to be meaningful when  $E - E' \ll E'$ , i.e. when the spectrum does not cover a wide energy range; therefore eq. (1) applies only to Auger spectra at relatively high energy. In summary we have two problems: (i) the determination of  $G(E)$  and (ii) the solution of the integral equation (1). The choice of  $G(E)$  will be discussed in section 3 while now we deal with the other topic.

The well-known convolution theorem makes the solution of (1) apparently very easy; in fact we have:

$$\tilde{N}(t) = \sqrt{2\pi} \tilde{A}(t) \tilde{G}(t), \quad (2)$$

where

$$\begin{aligned} \tilde{N}(t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{iEt} N(E) dE, \\ \tilde{A}(t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{iEt} A(E) dE, \\ \tilde{G}(t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{iEt} G(E) dE. \end{aligned} \quad (3)$$

Therefore the clean Auger spectrum is given by:

$$A(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-iEt} \frac{\tilde{N}(t)}{\tilde{G}(t)} dt. \quad (4)$$

Because of the random noise associated with *all* measurements the simple solution (4) appears to be disastrous: the high-frequency noise-components become much stronger than the measurement itself. This behaviour is hardly surprising, in fact the noise added to the *real*  $N(E)$  by the measurement operation is expected to be almost white, i.e. with a constant power spectrum. Then the regions where  $\tilde{G}(t)$  is small or zero introduce an enormous enhancement of the noise contribution to  $\tilde{A}(t)$  and hence strong oscillations in applying eq. (4). However this problem is a quite old one in restoring the true information contained in a noisy signal [3] and the well developed technique of the Bode-Shannon optimum filter [4] can be used to avoid it. This technique allows the determination of the best linear filter in the sense of root-mean-square (rms) error. It should be remarked that in any case the *true information* contained in a noisy signal *cannot be restored* because of the random nature of the noise. The only possibility is the determination of the best approximation to the true information. If we indicate with  $A_r(E)$  the restored spectrum, we have that:

$$\tilde{A}_r(t) = \frac{1}{\sqrt{2\pi}} \frac{\tilde{N}(t)}{\tilde{G}(t)} \tilde{\Phi}(t), \quad (5)$$

where  $\tilde{A}_r(t)$  and  $\tilde{\Phi}(t)$  indicate, in analogy with eq. (3), the Fourier transforms of  $A_r(E)$  and  $\Phi(E)$ , and the filter  $\Phi$  minimizes the rms error,  $e_{\text{rms}}$ ,

$$e_{\text{rms}} \equiv \int_{-\infty}^{+\infty} \epsilon_{\text{rms}}(E) \, dE \equiv \int_{-\infty}^{+\infty} \langle |A_r(E) - A(E)|^2 \rangle \, dE, \quad (6)$$

if it has the form [4]:

$$\tilde{\Phi}(t) = \frac{|\tilde{A}(t) \tilde{G}(t)|^2}{|\tilde{A}(t) \tilde{G}(t)|^2 + P(t)/\sqrt{2\pi}}, \quad (7)$$

$P(t)$  being the power spectrum of the random noise present in the actual signal  $N(E)$ . The symbol  $\langle \rangle$  indicates the average taken over the statistical ensemble of the noise. In eq. (7) we have implicitly assumed that the noise is well described by an additive stationary random-function. As we can see the *optimum filter* is expressed in terms of the true spectrum  $A(E)$  and therefore it *cannot be deduced exactly* from the experimental data. Various procedures have been suggested to obtain good estimates of  $\Phi$  [5], nevertheless a general method cannot be developed because the filter has to be adapted to the particular shape of the restoring spectrum and to the noise behaviour. In the following sections an application to Auger spectra will be given together with further details about the filter technique.

## 2. Comparison with van Cittert's method

As it is well known [1], the restoration of Auger spectra is often performed using a method proposed by van Cittert [6–8], therefore it is worthwhile to compare the method we have previously described with the more-standard van Cittert's approach. Such a method is based on an iterative procedure which allows one to determine the  $n$ th approximation,  $A_n(E)$ , to the Auger spectrum, starting from the  $(n-1)$ th one:

$$A_n(E) = A_{n-1}(E) + N(E) - \int_{-\infty}^{+\infty} G(E-E') A_{n-1}(E') \, dE', \quad (8)$$

$$A_0(E) \equiv N(E).$$

It is not obvious if in the presence of noise this formula produces a good approximation to  $A(E)$ . The only available information has been obtained through numerical simulations [9]. Nevertheless an analytical analysis of eq. (8) is extremely revealing. First of all we want to observe that, as already evidenced by Burger and van Cittert [8], eq. (8) has a closed solution for each  $n$  when the Fourier transform of this equation is taken. In fact, it is readily obtained that

$$\tilde{A}_n(t) = \tilde{N}(t) \frac{1 - H(t)^{n+1}}{1 - H(t)}, \quad (9)$$

where

$$H(t) = 1 - \sqrt{2\pi} \tilde{G}(t) \quad (10)$$

and  $\tilde{A}_n(t)$  indicates the Fourier transform of  $A_n(E)$ . It is interesting to observe that when  $|H(t)| < 1$  the limit of  $\tilde{A}_n(t)$  for diverging  $n$  exists and recovers the naive solution of eq. (4). If this is the case we can state that the van Cittert's method represents an elementary proof of the convolution theorem. In general, however, nothing can be said about the convergence of formula (8).

It should be remarked that eq. (9) contains all the drawbacks of eq. (4) as the denominator of both equations is the same. Therefore, van Cittert's method, for finite  $n$ , is equivalent to the use of a filter equal to  $1 - H(t)^{n+1}$ . As a consequence it is quite obvious that an optimum  $n$ , which minimizes  $e_{\text{rms}}$ , exists as actually found in ref. [9] through a numerical approach. As a final remark we observe that if the original noise contained in the experimental data is white, the noise which affects  $A_n(E)$  has a non-constant power spectrum, peaked in the regions where  $\tilde{G}(t)$  is small or zero. To evidence this fact we performed a numerical calculation of the rms error,  $\epsilon_{\text{rms}}(E)$ , as a function of  $E$ . The van Cittert method was applied 500 times to a model spectrum like that employed by Madden and Houston (see fig. 7 of ref. [9]) adding each time a different random noise to the "measured" spectrum. The result of such a calculation is given in fig. 1 where a well defined energy dependence of  $\epsilon_{\text{rms}}(E)$  is seen when the number of iterations,  $n$ , is small. On the other hand, when  $n$  increases  $\epsilon_{\text{rms}}(E)$  becomes almost constant but higher and higher.

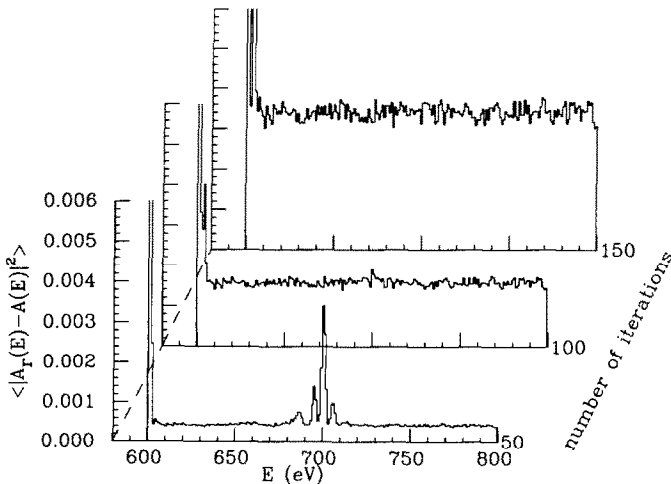


Fig. 1. Root-mean-square error (see eq. (6)) for a model spectrum restoration in the case of van Cittert's method. The result is shown as a function of the number of iterations.

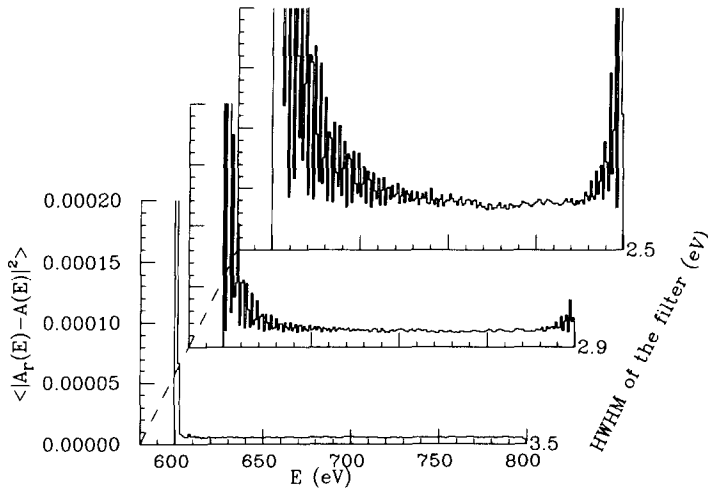


Fig. 2. As fig. 1 in the case of the gaussian-filter method (here  $A(E)$  represents the true signal convoluted with the gaussian function corresponding to the employed filter). The result is shown as a function of the filter HWHM.

In conclusion van Cittert's method is equivalent to a filter technique but introduces *uncontrolled* non-white noise so that spurious information may appear. This is the most serious drawback of van Cittert's approach together with the fact that the optimum value of  $n$  can be determined only using empirical methods.

As already said, the optimum filter can never be exactly known in practical cases and suitable approximations must be employed [5]. We propose to use a gaussian shaped filter. This choice is dictated by its simplicity, however it gives another advantage: the restored spectrum is not arbitrary distorted with respect to the true spectrum but it is the best-restored-spectrum convoluted with a known gaussian function (namely the Fourier transform of the filter). For comparison purposes we repeated the same calculation of fig. 1 using gaussian filters with three different HWHM's (half-width at half-maximum) comparing the restored spectrum with the corresponding gaussian-convoluted true spectrum. The results of this simulation are shown in fig. 2 where it is evident that even this simple filter gives a small and almost white rms error.

The gaussian filter can be improved at the cost of an increased complexity [10], but it will be shown in section 4 that it works fairly well when applied to real Auger spectra.

### 3. Choice of $G(E)$

As for the shape of  $G(E)$ , the current assumption [11,12] is to use the energy spectrum of backscattered electrons in the neighbourhood of the elastic

peak with an incident energy just below the Auger excitation threshold. This assumption appears to be meaningful if the probability for elastic backscattering is high compared to the probability of inelastic processes. If this is the case and indicating with  $B(E, E_0)$  the number of backscattered electrons at energy  $E$  when the impinging beam has energy  $E_0$ , and with  $L(E, E_0)$  the corresponding measured quantity, we have:

$$G(E, E_0) \simeq L(E, E_0),$$

$$\begin{aligned} L(E, E_0) &= \int_{-\infty}^{+\infty} B(E', E_0) R(E - E') dE' \\ &\simeq \int_{-\infty}^{+\infty} R(E') B(E - E_0 - E') dE', \end{aligned} \quad (11)$$

where  $B(E, E_0)$  has been assumed to depend on  $E - E_0$  only and  $R(E)$  is the instrument response. It is evident that the relationship (11) has the advantage of automatically correcting for the instrument response. We remark also that the above relationship holds if (i) the Auger and primary electrons interact with the solid in an identical manner and if (ii) the instrumental broadening is just the same for the two spectra.

Although the described approximation is quite standard it requires still some care [1,13]. We tried an experimental check of the above approximation in conditions close to those encountered when one studies LXX Auger spectra in transition metals and alloys. To this purpose we have measured the KLL Auger lines of Si in a  $\text{Fe}_{96}\text{Si}_4$  alloy. This system has been chosen because the concentration of Si is rather low and the alloy is known to be almost random, so that the atomic KLL lines can be assumed to be delta functions within the present resolution.

The experiment has been performed employing the PHI600 scanning Auger microprobe installed at ENEA Casaccia (Rome). The base pressure was  $4 \times 10^{-10}$  Torr. A cylindrical mirror analyzer (CMA) with 0.3% energy resolution was used and the excitation was provided by an electron beam. The sample was kept under vacuum for several days before the experiment was performed. Several spectra with different excitation energies,  $E_0$ , have been obtained and, according to Langeron et al. [14], a good peak-to-background ratio with  $E_0 = 20$  keV ( $E_0/E_a \simeq 12$ ,  $E_a$  being the Auger electron energy) has been found. Before and after the measurements the major contaminants like carbon, oxygen and nitrogen have been checked and their content has been reduced below the machine sensitivity by xenon sputtering. In fig. 3 the electron flux is shown as a function of kinetic energy. The complete set of KLL Auger lines of Si is evidenced ( $E_{\text{KL}_2\text{L}_2} = 1624$  eV,  $E_{\text{KL}_1\text{L}_2} = 1556$  eV and  $E_{\text{KL}_1\text{L}_1} = 1510$  eV). The spectrum of backscattered electrons at an incident energy near the Si K-level is reported in fig. 4.

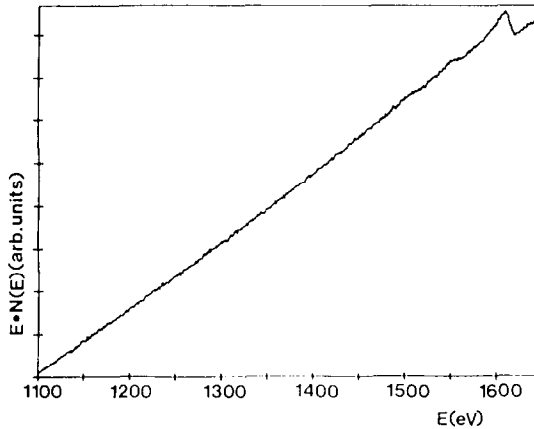


Fig. 3. Electron excited KLL Auger spectra of Si in a  $\text{Fe}_{96}\text{Si}_4$  alloy ( $E_0 = 20$  keV).

To check the validity of eq. (11) we have fitted the experimental data  $N(E)$  of fig. 3 with the following expression:

$$N(E) = \sum_{i=1}^p a_i E^{i-1} + \sum_{i=1}^3 b_i L(E - E_i, E_0). \quad (12)$$

The first term represents the primary background contribution simulated, as already said, by a low order polynomial while the second is the three Auger contributions obtained from eq. (1) assuming  $G(E) \approx L(E, E_0)$  and  $A(E) \approx \delta(E)$ . The coefficients  $b_i$  are proportional to the integral intensity of the KLL lines and  $E_i$  are the corresponding energies. The result of a rather good fit,

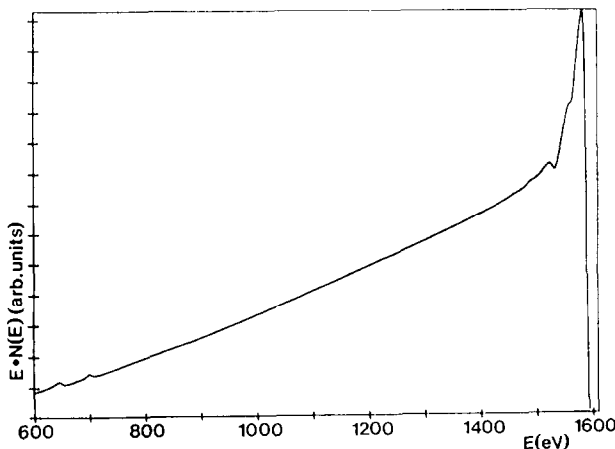


Fig. 4. Backscattered electron spectrum in a  $\text{Fe}_{96}\text{Si}_4$  alloy at incident energy  $E_0 = 1580$  eV.

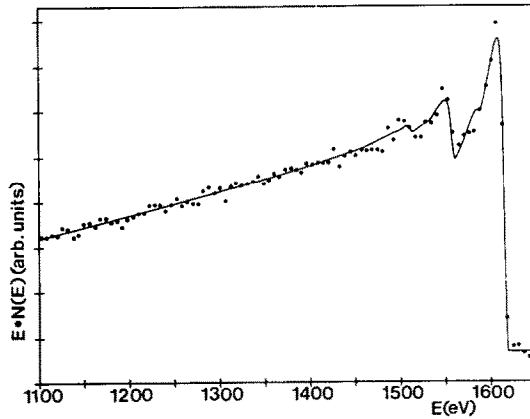


Fig. 5. Comparison of experimental data of fig. 3 after primary background subtraction (dots) and the fit explained in section 3 (solid line).

obtained with  $p = 3$ , is shown in fig. 5. We ascribe the slight difference between the fitted and experimental data to the fact that the inelastic loss near the elastic peak is greater (5%–10%) than the loss near the Auger peak. This behaviour appears to be in agreement with the information reported in ref. [12]. The parameters  $b_i$ , employed in the fit, are reported in table 1 where they compare favourably with those reported for pure Si [15].

#### 4. Restoration of Auger lines

To establish the real ability of the proposed procedure in recovering the appropriate information contained in an actual Auger spectrum, the gaussian-filter method has been applied to the LXX Auger spectrum of iron. In this particular case there are several Auger peaks present in a relatively small energy range (two hundred eV), some of these peaks involve the valence band while others are transitions between core states only. Moreover, there is a relatively strong line in the high kinetic energy region so that the correspond-

Table 1

Relevant parameters of the fit explained in section 3; the values of the parameters relative to the pure silicon are taken from experimental data of the authors (not published)

Parameter	Present	Pure Si
$b_{KL_2L_2}$	100	100
$b_{KL_1L_2}$	19	18.5
$b_{KL_1L_1}$	4	4.3



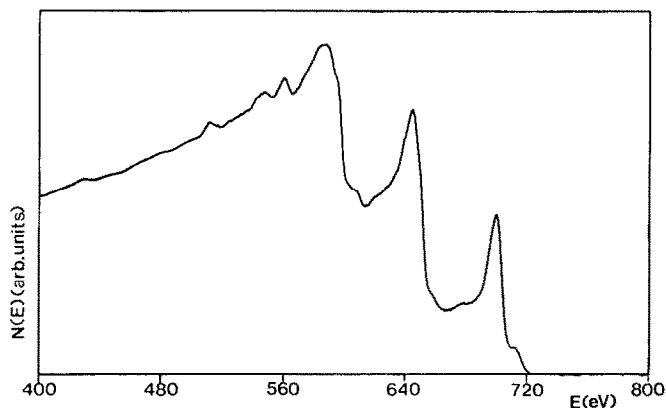


Fig. 6. Electron excited Auger spectrum of Fe in the region of the  $L_{2,3}$  core states ( $E_0 = 3$  keV).

ing inelastic loss is expected to affect the shape of the other lines located at lower energy.

The measurements have been performed with the same experimental arrangement described in the case of  $Fe_{96}Si_4$  alloy. The sample was pure polycrystalline iron. As already done in the case of  $Fe_{96}Si_4$ , the sample contamination was kept as low as possible and several different runs have been performed in the energy range 400–800 eV. The excitation energy was 3 keV, appropriate for the present Auger energy. More than  $10^7$  counts have been obtained per energy channel (0.2 eV) and different runs were equal within the statistical error. The experimental data, after averaging of all different runs and after primary background subtraction, are reported in fig. 6. The primary electron background has been modeled by a third degree polynomial as in the case of  $Fe_{96}Si_4$  alloy, where such a procedure worked

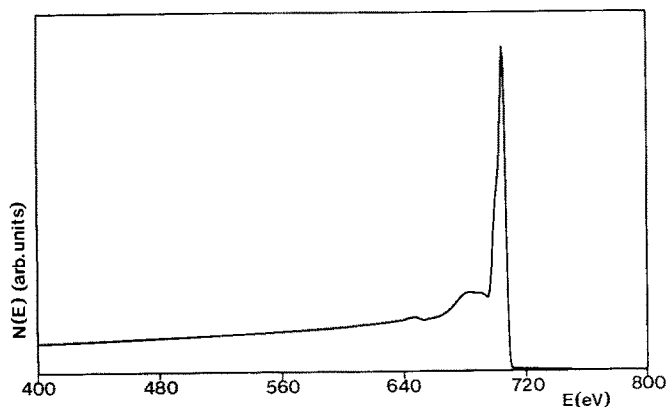


Fig. 7. Backscattered electron spectrum of Fe at an incident energy  $E_0 = 700$  eV.

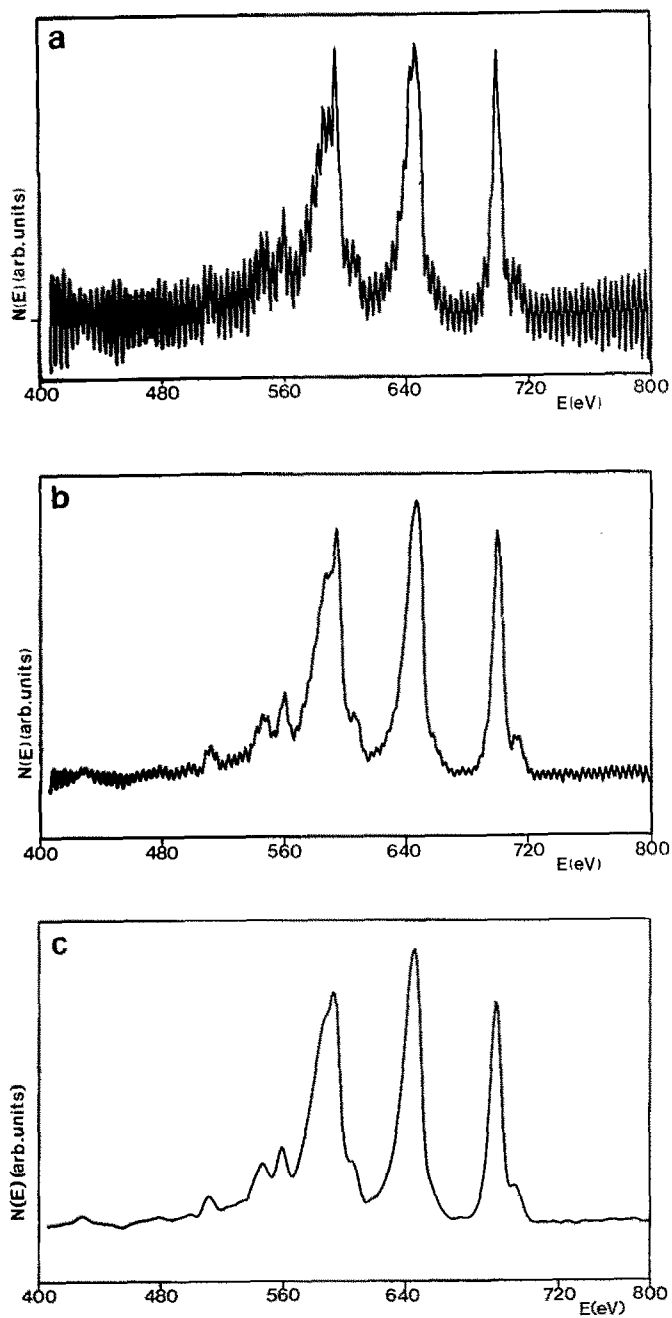


Fig. 8. Restoration result of the spectrum of fig. 6 obtained with a gaussian filter. The value of the HWHM is 1.8 eV in (a), 2.2 eV in (b) and 2.9 eV in (c).

successfully (to check this polynomial approximation we measured, with lower statistics, the Fe spectrum also in the energy range 100–800 eV). Finally, to determine  $G(E, E_0)$ , according to eq. (11), the backscattered electron flux has been determined at  $E_0 = 700$  eV and is shown in fig. 7.

The restoration of the iron spectrum has been performed employing the simple gaussian filter described in section 2. The results are reported in figs. 8a–8c for three different choices of the filter HWHM. As we can see an HWHM of 2.9 eV is perfectly adequate to the purpose of obtaining a virtually loss- and noise-free spectrum. It should be remarked that the experimental spectrum so obtained can always be quantitatively compared with a theoretical estimate convoluted with the known gaussian resolution [16].

Although the restored spectrum looks quite nice, one has to remember that the quality of the original data is very important: in fact, the higher the noise present in the original data, the broader the filter should be, thus resulting in a worse restored spectrum.

## 5. Conclusion

As a conclusion we want to recall the most important features of the restoration procedure we have described. First of all this procedure works independently of the shape of the experimental spectrum assuring one and only one restoration result that is the true result convoluted with a well defined gaussian. Moreover a reduced numerical effort is needed, thus allowing an almost real-time data analysis. Low signal-to-noise ratio data can be restored without particular problems though the noise level characterizes the amount of information which can be extracted from the restored spectrum.

Therefore we can state that a gaussian filter approach to the restoration problem is very flexible while the more-standard van Cittert's method, which belongs to the same class of filtering methods, shows little adaptability and introduces spurious and uncontrolled information.

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