

The quality of X-ray microanalysis in the ultra-soft X-ray region

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1967 Br. J. Appl. Phys. 18 1033

(<http://iopscience.iop.org/0508-3443/18/8/301>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 128.104.1.220

The article was downloaded on 07/07/2011 at 18:45

Please note that [terms and conditions apply](#).

The quality of X-ray microanalysis in the ultra-soft X-ray region

C. A. ANDERSEN

Applied Research Laboratories Inc., Hasler Research Center, Goleta, California, U.S.A.

MS. received 7th October 1966, in revised form 12th January 1967

Abstract. The quality of a microanalysis by means of x-rays may be defined in terms of the degree of spatial resolution attained, the sensitivity of detection, the precision of the measurement and the accuracy of the measurement. These parameters are discussed in relation to the ultra-soft x-ray region. The ability to perform a quantitative analysis receives special attention, and is found to be greatly affected by the nature of the chemical bonding of the specimen, the correction theory used, and the availability of accurate mass-absorption coefficient data.

1. Introduction

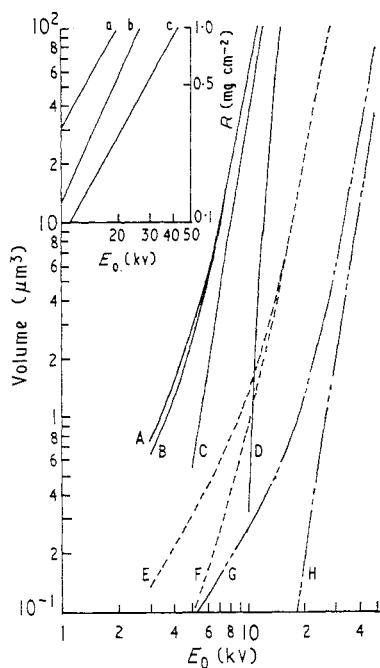
It is the purpose of this paper to discuss and delineate the parameters which affect the quality of microanalysis in the ultra-soft x-ray region, in order to establish a general level of this quality for comparison with that found in the more familiar hard x-ray region. The quality of a microanalysis by means of x rays may be defined in terms of the degree of spatial resolution attained, the sensitivity of detection, the precision of the measurement and the accuracy of the measurement. Spatial resolution is determined by the volume of the sample which, through excitation by the primary electron beam, contributes to the analysis. The size of the excited volume is a function of the range of the primary electrons, and hence their accelerating potential, and the excitation potential of the particular characteristic x-ray lines utilized for the analysis. Sensitivity of detection is commonly considered in two categories. The first, the weight-fraction or relative detection limit, describes the smallest weight fraction of the analytical element detectable in the sample, irrespective of the volume which must be excited to achieve this limit. The second, the absolute detection limit, gives the smallest number of atoms necessary for the analysis. The first limit depends on the integrated intensity received from the analytical line and its associated background, while the second depends on the weight-fraction detection limit and the volume analysed. The precision of an analysis describes the limits of reliability which can be assigned to a reported value in consideration of the errors involved in the measurement itself. Included in these errors are such factors as instrumental drift, x-ray statistics, differences in surface contamination and differences in unseen sub-surface composition. The accuracy of the measurement is a description of how close the results of the quantitative analysis are to the true composition. Accuracy in electron-probe microanalysis is, therefore, dependent on the validity of the correction procedure employed, the quality of the reference standards utilized and the imposed instrumental analysis conditions. These parameters defining the quality of microanalysis are discussed in their relation to the ultra-soft x-ray region.

2. Spatial resolution

The analysis of smaller and smaller volumes is a fundamental goal of microanalysis. This can best be achieved, while staying within the bounds of x-ray emission microanalysis as commonly employed, by reducing the accelerating potential of the primary electron

† This paper was presented in part at the First American National Conference on Electron Probe Microanalysis, held at College Park, Maryland, U.S.A., in May 1966.

beam. The volume of material contributing to the analysis due to direct electron excitation is shown in figure 1 as a function of the accelerating potential E_0 , the excitation potential E_c of the characteristic x-ray line under investigation and the density ρ of the sample (Andersen and Hasler 1967). The curves shown have been drawn for a range of densities commonly encountered in the fields of biology, mineralogy and metallurgy. The influence of the diameter of the electron probe is indicated in the curves given for $\rho = 8.92$ (curves G and H). All the other curves are drawn for an electron probe $1 \mu\text{m}$ in diameter.



Main figure		
Curve	E_c (kv)	ρ (g cm ⁻³)
A	0	0.42
B	1.07	0.42
C	4.04	0.42
D	9.66	0.42
E	0	2.40
F	4.04	2.40
G	0	8.92
H	0	8.92

Inset figure

a Maximum depth of x-ray production
 b Diameter of x-ray production volume
 c Mean depth of x-ray production

Figure 1. Volume of x-ray production as a function of accelerating potential E_0 , sample density ρ and excitation potential E_c of the analytical line (from Andersen and Hasler 1967). For curve H the probe diameter is infinitesimally small, for all the other curves it is $1 \mu\text{m}$.

It is obvious from this figure that the volume contributing to the analysis is a rapidly changing function of accelerating potential for a given density, and that the use of low accelerating potentials will greatly reduce the size of the volume excited. Considering the generally large accelerating potentials commonly employed, improvements in spatial resolution through reduction of accelerating potential can be as large as 100 times or more, depending on sample density. For the analysis of low-density specimens this approach is essential. Analytical volumes of a few cubic micrometres, equivalent to those at present attainable in high-density specimens, can be achieved in samples with densities as low as 0.4 (typical of dry tissue) at an accelerating potential of 5 kV .

Figure 1 also shows that spatial resolution can be increased for a particular element by using an accelerating potential close to the critical excitation potential of one of its characteristic x-ray lines. Although this technique produces very small analytical volumes for the element in question, it also produces the generally undesirable consequence that the characteristic x-ray emission of other elements of lower critical excitation potential will come from comparatively large volumes, resulting in the reported elemental analyses not representing the same volume. For example, it can be seen in figure 1 that at 11 kV in dry tissue a Zn analysis using the Zn $K\alpha$ line ($E_c = 9.66 \text{ kV}$) originates from a volume of about $2 \mu\text{m}^3$, but that the analysis of Na using its $K\alpha$ line ($E_c = 1.07 \text{ kV}$) originates from a volume of $75 \mu\text{m}^3$. This situation can be improved by using the $L\alpha$ line of Zn ($E_c = 1.02 \text{ kV}$) and

reducing the accelerating potential still further. At an accelerating voltage of 5 kv the volumes contributing to the analyses of Zn and Na as well as all the lighter elements will be about $2 \mu\text{m}^3$.

Generally then, from the above discussions it is clear that in order to attain the best possible spatial resolution, and yet maintain the equality of the spatial relationships of the elemental analyses, the longest-wavelength characteristic x-ray lines of the elements which are detectable should be used at the lowest accelerating potential compatible with the other basic aims of the analysis. This consideration is especially important when dealing with the light elements ($Z < 12$), which have low critical excitation potentials (of the order of 1 kv or less).

3. Detection sensitivity

The ideal in microanalysis is to be able to detect very small numbers of atoms of an element in minute volumes. The weight-fraction detection sensitivity of an element is determined by the intensities of the characteristic x-ray line and the associated background radiation. These intensities are in turn dependent on the accelerating potential used, the primary electron-beam current, the integration period, the efficiency of the x-ray diffractor and detector used in the x-ray detection system, and the matrix in which the element is found. The absolute detection limit is determined by the weight-fraction detection sensitivity and the volume of material excited. It is therefore dependent on spatial resolution and accelerating potential, as discussed in §2.

All the above interrelated parameters are very important to the degree of detection sensitivity attainable and are limited by practical considerations. In order to indicate the detection sensitivities attainable in practice in the ultra-soft x-ray region the following operational parameters have been employed. An Applied Research Laboratories EMX with a 52.5° take-off angle was used. The instrument was relatively noise-free (20 counts per 100 sec) and the contamination rate on the sample under electron bombardment was low enough to permit 100 sec integrations at reasonable beam currents without the deposition of detectable amounts of carbon. X rays of wavelengths longer than 25 \AA were diffracted from a lead stearate decanoate soap-film pseudo-crystal and wavelengths shorter than this with a potassium acid phthalate (KAP) crystal of Johann and Johansson geometry. A proportional flow counter fitted with an ultra-thin nitrocellulose window and an electron deflector was operated at atmospheric pressure with P_{10} gas in conjunction with a pulse-height selector. An integration period of 20 sec and a sample current of $0.05 \mu\text{A}$ were used in the study of minerals and tissue specimens, while a 100 sec integration period and a sample current of $0.10 \mu\text{A}$ were used in the studies of metals, which can generally take greater heat loads for longer periods of time without apparent material alteration (most metals are able to withstand even higher sample currents). With these parameters fixed, only the matrix material and the accelerating potential are left as major variables.

The accelerating potential is extremely important not only because it determines the volume of material analysed, and therefore directly affects the absolute detection limit, but also because the observed intensities of both the characteristic line and the background due to the x-ray continuum are functions of the accelerating potential. The efficiency of production of a characteristic x-ray line is proportional to the difference between the accelerating potential and the critical excitation potential of the line raised to an exponential power of about 1.6, while the efficiency of production of the background is proportional to the same difference raised to the power 1.0. This indicates that if there were no x-ray absorption of the generated x-rays the weight-fraction detection sensitivity would continually increase with increasing accelerating potential. In the ultra-soft x-ray region, however, x-ray absorption is very important in view of the large mass-absorption coefficients normally encountered. The increase in absorption with increasing accelerating potential tends to cancel the increase in production efficiency, with the result that at a particular accelerating potential, determined by the value of χ ($\chi = (\mu/\rho) \text{ cosec } \theta$) for the characteristic line in the sample under study, the observed intensity will reach a maximum, and thereafter decline with further increase in the accelerating potential. To demonstrate

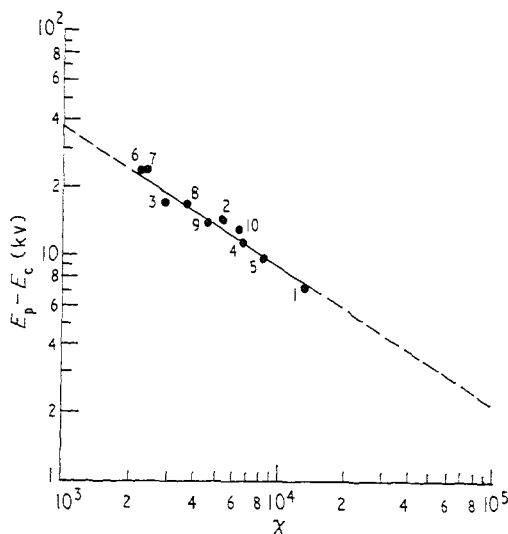


Figure 2. The most efficient accelerating potential as a function of χ . The numerals by each point refer to the 'point nos.' in table 1.

the importance of this effect in the ultra-soft x-ray region ($E_c \sim 1.0$ kv or less), figure 2 gives the experimentally determined value of the accelerating potential E_p which produces the maximum observed intensity as a function of χ for various samples. It is evident that, for the values of χ usually encountered in this wavelength range, low accelerating potentials are generally required to produce maximum intensity. This means that, in effect, each characteristic x-ray line will have a different E_p in each matrix of significantly different χ , and therefore a different maximum detection sensitivity in each matrix. The sample also affects the detection sensitivity through the background intensity due to the x-ray continuum, which generally increases with increasing average atomic number of the sample. E_p has been plotted by subtracting the critical excitation potential E_c of the characteristic x-ray line studied. The values of the mass-absorption coefficients (μ/ρ), the elements and the samples used in determining E_p and χ are given in table 1.

Table 1. Values used to determine E_p and χ in sample AB (figure 2)

Point no. (figure 2)	Element A	E_c (kv)	Sample AB	E_p (kv)	$(\mu/\rho)_A^A$	$(\mu/\rho)_B^A$
1	C	0.283	Fe ₃ C	7.5†	2280 ¹	11000 ²
2	O	0.531	SiO ₂	15†	983 ³	8040 ³
3	C	0.283	graphite	17.5†	2280 ¹	—
4	C	0.283	diamond	11.7‡	2280 ¹	—
5	N	0.399	BN	10†	1440 ³	13470 ³
6	Na	1.08	NaCl	25†	580 ⁵	2578 ⁴
7	Cu	0.933	Cu	25†	1871 ⁶	—
8	Fe	0.708	Fe	17.5†	2950 ⁷	—
9	Na	1.08	tooth§	15†	580 ⁵	3648 ⁴
10	Fe	0.708	Fe ₂ O ₄	13.8†	2950 ⁷	10740 ³

† Measurements made by author with cosec $\theta = 1.260$.

‡ Measurement taken from Duncumb and Melford (1967) with cosec $\theta = 2.924$.

§ In this case $(\mu/\rho)_B^A$ is actually $(\mu/\rho)_{\text{matrix ABC}}$.

Sources of (μ/ρ) :

1, Ogier *et al.* (1964); 2, Duncumb and Melford (1967); 3, Henke *et al.* (1957); 4, Heinrich (1966); 5, extrapolation of data given by Heinrich (1966); 6, Cooke and Stewardson (1964); 7, extrapolation of data given by Cooke and Stewardson (1964).

The weight-fraction detection limit is defined here as the concentration of the element required to produce an intensity larger than the intensity of the background at the position of the analytical line by an amount equal to three times the standard deviation of the background intensity. This value gives 99.7% confidence that an x-ray signal detected at that intensity level at that wavelength is due to the presence of the element. In consideration of this definition and the discussions on the dependence on accelerating potential of the production efficiency of characteristic and background x rays, it is clear that the best weight-fraction detection limit occurs close to E_p and, in most cases in the ultra-soft x-ray region, that this is a rather low value of the accelerating potential. The absolute detection limit is the number of atoms or grammes of the element detectable and is calculated by multiplying the weight-fraction detection limit by the analysed mass. The analysed mass is the product of the excited volume V and the sample density ρ . The size of the excited analytical volume, which is a function of accelerating potential, plays a dominant role in determining the number of grammes detectable, producing the result that the best absolute detection limits are also found at low values of the accelerating potential.

Microanalysis is basically concerned with the study of chemical heterogeneity on a minute scale, that is to say with small unevenly distributed groups of atoms. Detection sensitivity should therefore be thought of in terms of detection of the smallest number of atoms of an element in the smallest possible volume, and it becomes of primary importance to consider the absolute detection limit. The weight-fraction detection limit gives no information on the size of the excited volume or mass of the sample required to attain the stated limit. The best weight-fraction detection limit may actually require the localized grouping of a large number of atoms when considered as a weight fraction of a large analysed mass. The best absolute detection limit, however, gives the smallest number of atoms detectable in the minimum required volume. It is possible to analyse smaller volumes by further reducing the accelerating potential, as may be required for reasons of better spatial resolution, but not for the same minimum number of atoms of the element. Each characteristic line of an element will, in principle, have a different value of the absolute detection limit for a given set of conditions. For the light elements ($Z < 12$) only the $K\alpha$ spectra need be considered since these lines are the most intense at all accelerating potentials. For elements of atomic number higher than 12 both the $L\alpha$ and the $K\alpha$ spectra should be considered. These two lines compete to produce the best absolute detection limit as the accelerating potential, sample composition and the detection system efficiency for each line are changed. A good example of this competition is given by the first transition metals, where the $L\alpha$ spectra fall within the ultra-soft x-ray region. Figure 3 gives typical values of the absolute detection limits for the $L\alpha$ and $K\alpha$ lines of Fe and Zn and for the $K\alpha$ lines of some of the light elements in various types of matrices for the conditions of analysis previously stated. Diffraction of the $K\alpha$ lines of Zn and Fe was accomplished with a fully-focusing LiF crystal. The Zn $L\alpha$ and Zn $K\alpha$ lines compete very effectively with each other in matrices where the mass-absorption coefficient for the $L\alpha$ line is low. For the Fe $L\alpha$ and Fe $K\alpha$ lines, where the wavelength of the $L\alpha$ line is considerably longer, the mass-absorption coefficients higher and the detection system efficiency poorer than is the case for the Zn $L\alpha$ line, the competition is not as even, and the best absolute detection limits can be attained by using the $K\alpha$ line at an accelerating potential slightly larger than the critical excitation potential of Fe $K\alpha$. This technique will suffer, however, from a loss of spatial equality if other elements are analysed in conjunction with Fe, as has been discussed previously. For this reason it may be better in this case to sacrifice a factor of about 10 in absolute detection capability and use the Fe $L\alpha$ line at a lower accelerating potential. With further increases in the wavelength of the L lines the detection capabilities become steadily poorer.

As can be seen in figure 3, the $K\alpha$ lines of the light elements in general provide better detection sensitivities than the L spectra of heavier elements in the same wavelength region. A contributing factor here is that the $K\alpha$ fluorescent yields are greater than those of the $L\alpha$ lines. Also, in some cases the efficiency of the detection system for a certain line is particularly good. C $K\alpha$, for example, is transmitted through the thin window of the detector with relatively small loss of intensity as compared with Ca $L\alpha$ and Cr $L\alpha$, which are adversely

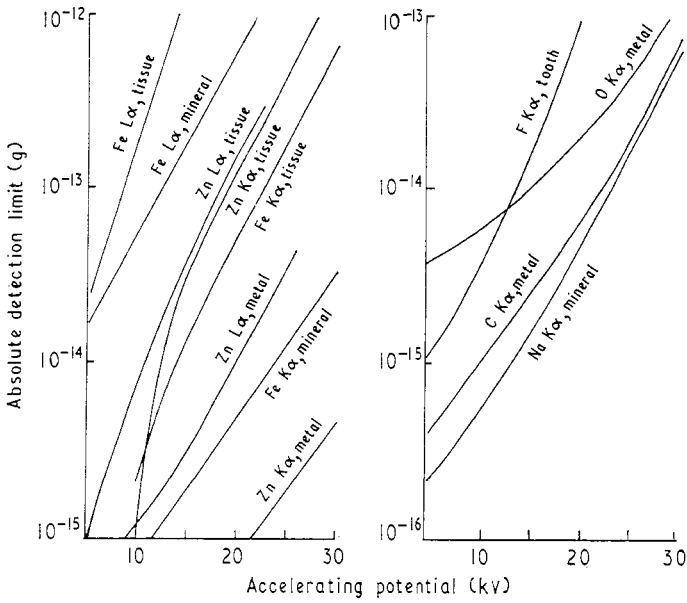


Figure 3. Absolute detection limits.

affected by the C and O absorption edges of the window. It is evident that the ability to detect an element using a line in the ultra-soft x-ray region is a very complicated function of the sample, the accelerating potential, the fluorescent yield of the line and the detection system. It can also be a function of the contamination rate and the rate of generation of spurious counts of the individual instrument. The x-ray diffractors for the detection system are being continually improved, and should eventually lead to much better detection capabilities. For example, Nicholson and Hasler (1965) have demonstrated absolute detection limits at an accelerating potential of 5 kv using a diffraction grating in a micro-probe of about 10^{-15} g for O in a mineral specimen and 10^{-14} g for the very long K α wavelength (114 Å) of Be in a low-absorption matrix under the conditions previously specified for mineral and tissue analysis. The weight-fraction detection limits in these two cases were about 0.13 and 1.30% respectively. The experimentally determined weight-fraction detection limits used to calculate the absolute detection limits of figure 3 are given in figure 4.

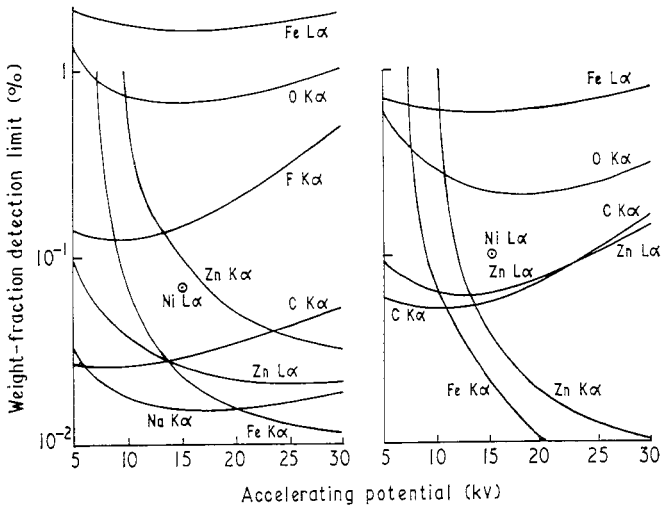


Figure 4. Weight-fraction detection limits.

4. Precision of analysis

The relative precision of the analysis from point to point on a specimen is very important in microanalysis, and is usually considered to be very good with the electron probe. It is affected by such factors as instrument stability, detector linearity, statistical fluctuations in the x-ray intensity and differences in surface contamination, topography and sub-surface composition. In the ultra-soft x-ray region, precision is no more affected by instrumental drift than in the harder x-ray region, unless low accelerating potentials are used when fluctuations in probe diameter may be more severe. Probe displacement by stray fields or sample charge-up may also be larger at low accelerating potentials. Detector linearity should be no more critical in the ultra-soft region than in the harder region if proper attention is paid to opening the window of the pulse-height selector (if one is used) sufficiently to accommodate the wider pulse-height spectrum associated with the very long wavelengths.

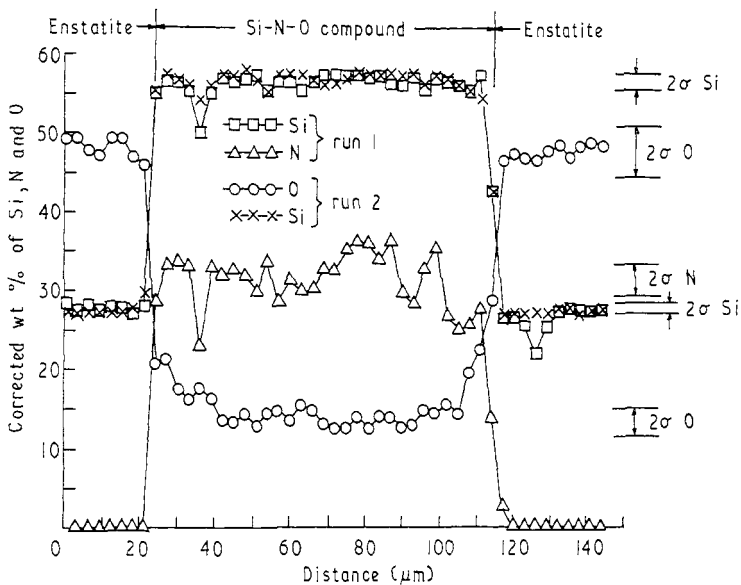


Figure 5. Point integration traverse across grain of $\text{Si}_2\text{N}_2\text{O}$ (sinoite) showing $\pm 2\sigma$ statistical variation levels.

Detector linearity may even be improved since the lower counting rates encountered reduce the effect of pulse-height shrinkage and coincidence loss in the detector. The low intensities of the ultra-soft x-ray spectrum do produce generally poorer precision per unit integration period. The precision of an individual measurement related only to fluctuations in the counting statistics is given by the equation $\sigma(\%) = 100/N^{1/2}$, where N is the total number of counts observed. An example of the type of precision experienced in practice with the very long wavelengths is given by the mineral analysis shown in figure 5, where O and N were determined by point integration across the mineral grain (Andersen *et al.* 1964). The precision of an individual O analysis at the $\sigma = 68\%$ confidence level is about 7%, while that of the short-wavelength Si measurement is slightly less than 1% under the conditions described for mineral analysis and at an accelerating potential of 5 kv. Increasing the integrated intensity by a factor of 3.75 reduced the Si precision to about 0.5%, as compared with 3% for N. The condition of the surface is important in the ultra-soft x-ray region because of the generally large absorption coefficients encountered. Differences in surface contamination layers or topography may cause differences in absorption from point to point. The composition of the contamination layer also becomes important if elements in the contamination layer are sought in the specimen. Surface layers become more important as lower electron accelerating potentials are used and the average depth of

x-ray production is moved closer to the surface. However, by the same reasoning, these same lower accelerating potentials will improve the precision from point to point with respect to unseen sub-surface composition changes.

5. Accuracy of analysis

The accuracy of analysis in the ultra-soft x-ray region is affected by (i) a possible inability to resolve the characteristic x-ray spectra of member elements of a compound, (ii) the large changes in the distribution of intensity between the various lines of the characteristic long-wavelength spectra of an element with changes in chemical bonding, (iii) the lack of a complete understanding of the correction theory to be used in this wavelength region and (iv) a general lack of well-determined mass-absorption coefficients and atomic-number correction parameters.

The accuracy of a qualitative identification of an element and of a quantitative determination of the concentration of the element present in a sample are dependent on the ability to resolve the characteristic x-ray spectrum of the element in question from the spectra of companion elements and to measure accurately the intensity of a suitable line in its spectrum. The ability to do this in the ultra-soft x-ray region is hampered in many cases by the generally poorer resolving properties of the large *d*-spacing diffractors used, especially the soap-film pseudo-crystals, and by the poorer resolving properties of the proportional detector for low-energy x rays. An additional complication occurs in the spectrum of a compound of the heavier metals due to the rather large number of characteristic lines in their L spectra. The L spectra of the first transition metals span the wavelength region from 36 to 12 Å, each element having five major lines. Some of these lines or their higher-order reflections cannot be resolved from the K spectra of the light elements, for example the first orders of V $L\beta_1$ from O $K\alpha$ and Ti $L\epsilon$ from N $K\alpha$. Also it may not always be possible to completely resolve the $L\alpha$ of one of these metals from the $L\epsilon, \eta$ lines of the metal of the next higher atomic number. These are complications not ordinarily experienced in analysis of the transition metals in the hard x-ray region when employing their relatively simple K spectra.

The emission concentration proportionality first proposed by Castaing (1951, 1960) is of fundamental importance to quantitative analysis. The assumption states that the x-ray intensity of an 'important characteristic line' of an element in a compound is related to its mass concentration as the x-ray intensity of the 'same characteristic line' in a standard is related to its mass concentration in the standard, when the two are compared under identical operating conditions and neglecting the effects of absorption, secondary fluorescence and atomic-number differences. This assumption is valid in the hard x-ray region, where the inner shell transitions giving rise to the characteristic spectra commonly utilized for analysis are well shielded from the influences of chemical bonding by succeeding shells of electrons. This assumption, however, is not generally true in the ultra-soft x-ray region, where the electron shells giving rise to the characteristic lines used are directly affected or actually involved in the chemical bonds. In these cases the relative intensity distribution among the various characteristic lines of an element is altered by the character of the chemical bond. This effect is well illustrated by the L spectra of the first transition metals, where it is no longer possible to deduce the mass concentration of an element in a compound by comparing the intensity emitted in one of the element's characteristic L lines with that emitted by any standard containing a known amount of that element.

The first intensity ratios of Fe in four common compounds, using its three most intense L lines and either pure Fe or Fe_3O_4 as a standard are given in table 2. The data were taken at 15 kv and corrected for detector coincidence losses and background. Fluorescence and atomic-number effects are considered to be small because of the low fluorescent yields of these lines and the similarity of the average atomic numbers of the compounds. The correction for absorption does not significantly alter the large relative errors encountered as a consequence of the failure of the primary assumption discussed above and was not applied so as not to confuse the pattern of these errors. Obviously in this wavelength region more is required of a standard used in the study of the transition metals than just the normal requirement of having a well-known homogeneous composition. The standard must

Table 2. Quantitative analysis with Fe L spectra

Fe line	Standard	Sample			
		Fe ₃ O ₄	Fe ₂ O ₃	FeS ₂	Fe ₃ C
L α _{1, 2}	100% Fe	25.4	23.1	45.7	97.8
	Fe ₃ O ₄	—	65.7	130.0	278.2
L β ₁	100% Fe	136.6	138.7	73.7	99.1
	Fe ₃ O ₄	—	73.5	39.1	52.5
L ι	100% Fe	30.7	28.4	23.1	79.3
	Fe ₃ O ₄	—	67.0	54.4	187.2
Average of 3 lines	100% Fe	64.2	63.4	47.5	92.1
	Fe ₃ O ₄	—	68.7	74.5	172.6
True Fe concentration		72.36	69.94	46.55	91.62

resemble the sample in the character of its chemical bonding. Pure Fe is a poor standard with which to study Fe₂O₃, but an Fe₃O₄ standard is adequate. For example, using the L α line and Fe₃O₄, the mass concentration of Fe derived in Fe₂O₃ is 65.7%. After correction for absorption this becomes about 67.5%, resulting in a relative error of 3.5%. Pure Fe is a better standard for Fe₃C and FeS₂. The average of the three lines improves the analysis with both standards. The large changes in the relative distribution of intensity in the L spectra of the first transition metals suggests a possible way of improving the accuracy of determining the nature of the chemical bond of an element in an unknown compound. Measuring the relative intensity ratios of the L lines rather than their wavelength shifts may be experimentally more accurate in this region, where the intensities are low and the resolution capabilities of the crystals poor.

Quantitative analysis in the ultra-soft x-ray region is further complicated by incomplete understanding of the correction theory to be used in this region and by a lack of the fundamental constants required for quantitative correction. Mass-absorption coefficients are notably lacking and in this wavelength region, considering the magnitude of the typical absorption coefficient, this can lead to very large errors. The effect of the mass-absorption coefficient can be diminished by reducing the path length over which the generated x rays must travel in the sample. This is best accomplished in a particular instrument by reducing the accelerating potential and bringing the source of x rays closer to the surface. Errors can still be large, however, and it is essential to have some knowledge of the mass-absorption coefficients if the standard and sample are different in composition by any significant degree and if quantitative accuracies typical of those attainable in the hard x-ray region are sought. In this regard, until better measurements of μ/ρ for this wavelength region are available, a rough idea of χ for the wavelength and sample under study may be gained directly from an experimental determination of E_p and the use of a curve such as that shown in figure 2. E_p is determined experimentally by observing the variation of intensity of the line with increase in accelerating potential under conditions of constant sample current. The curve has a basis in the interrelationship between the efficiency of x-ray production, which increases with increasing accelerating potential as approximately $(E_0 - E_c)^{1.63}$, and x-ray absorption, which also increases with increasing accelerating potential as the average depth of x-ray production is pushed deeper into the sample. The curve predicts values of χ for C K α in graphite and Fe₃C which can be substituted in the following example with little change in the final absorption correction factors.

One of the basic problems confronting quantitative analysis in the ultra-soft x-ray region is incomplete understanding of the correction procedure to be used. Many special problems are posed by such unknowns as the effect of the large over-voltages commonly applied (at 5 kv the accelerating potential is more than fifteen times the critical excitation potential of C K α) and the large amounts of absorption ordinarily encountered. The effect of these on the correction scheme adopted from the hard x-ray region as based on Philibert's model of electron scattering is unknown. These points have been discussed recently by Duncumb and Melford (1967). In their study four basic approaches to quantitative correction were investigated. These consisted of a thin-film model which essen-

tially limits all observable x-ray production to the specimen surface layer, the Philibert model commonly employed in the hard x-ray region where the ionization contribution at the surface is zero ($\phi(0) = 0$), a Philibert model corrected to incorporate the large contribution to the observed intensity by ionization occurring at the surface ($\phi(0) \neq 0$), and a Monte Carlo method in which a large number of electrons are followed through their individual ionization histories. Duncumb and Melford recommend the Monte Carlo method. The same four approaches were studied in this investigation of quantitative accuracy, using the carbon-in-iron system. This system was chosen because well-analysed specimens are available, and because the mass-absorption coefficients and atomic-number correction parameters have been established, the latter from the work of Duncumb and Melford (1967). The results of the study are given in table 3 for accelerating potentials of 5 and 10 kv. C was analysed in Fe_3C (6.7% C) using standards of 100% pyrolytic graphite and a solid solution of carbon in Fe (1.64% C). The solid solution standard gives good results with simply the first intensity ratio corrected for background, whereas the graphite standard produces results which are too large at 5 kv and too small at 10 kv. Applying the atomic-number correction (0.76 at 5 kv and 0.82 at 10 kv) and then the various absorption corrections produces the results shown. The thin-film model fails, presumably because the value of χ (2873 C $\text{K}\alpha$ in graphite) is too low. This is in accordance with the model as proposed by Duncumb and Melford (1967). The Philibert models, both corrected for the contribution of ionization at the surface and uncorrected, give essentially identical results.

Table 3. Quantitative analysis of C in $\text{Fe}_3\text{C}\dagger$

	5 kv	Relative error	10 kv	Relative error
Observed weight per cent 1.64% C in Fe standard	6.4	4.5	6.3	6.0
Observed weight per cent graphite standard	8.1	21.0	4.5	33.0
Atomic number correction‡	6.2	7.5	3.7	45.0
Absorption correction:				
1 Thin-film model	19.3	188.0	11.4	70.0
2 Philibert, $\phi(0) = 0$	9.0	34.0	7.8	16.0
3 Philibert, $\phi(0) \neq 0$	9.0	34.0	7.7	15.0
4 Monte Carlo	7.1	6.0	6.7	0

† True concentration 6.7%.

‡ Atomic number correction from Duncumb and Melford (1967).

1 Thin-film approximation from Duncumb and Melford (1967).

2 Philibert (1963) with Duncumb and Shields (1966) modification.

3 Philibert (1963) full expression with Duncumb and Melford (1967) modification.

4 Interpolation of $f(x)$ curves given in Duncumb and Melford (1967).

The Monte Carlo method shows the best agreement, although in this case the absorption correction factors $f(\chi)$ had to be interpolated and extrapolated from curves given by Duncumb and Melford and are probably not extremely accurate. Too much weight should not be given to the smaller relative error in the 10 kv analysis since the precision of the analyses at the 95% confidence levels, incorporating the statistical fluctuations in the line and background of both sample and standard, is $\pm 0.4\%$ C by weight or a 6% relative error. From this study it is obvious that, if samples and standards are significantly different, of the quantitative correction schemes thus far suggested for the ultra-soft x-ray region only the Monte Carlo method produces results which approach being comparable with those commonly attained in the hard x-ray region. Quantitative analysis can be very good if the samples and standards are similar in chemical composition.

References

- ANDERSEN, C. A., and HASLER, M. F., 1967, *Proc. 4th Int. Congr. on X-ray Optics and X-ray Microanalysis, Paris, 1965* (Paris: Hermann), in the press.
- ANDERSEN, C. A., KEIL, K., and MASON, B., 1964, *Science*, **146**, 256-7.
- CASTAING, R., 1951, *Thesis, Univ. Paris* (Paris: O.N.E.R.A.), No. 55.
- 1960, *Advanc. Electron. Electron Phys.*, **13**, 317-86.
- COOKE, B. A., and STEWARDSON, E. A., 1964, *Brit. J. Appl. Phys.*, **15**, 1315-9.
- DUNCUMB, P., and MELFORD, D. A., 1967, *Proc. 4th Int. Congr. on X-ray Optics and X-ray Microanalysis, Paris, 1965* (Paris: Hermann), in the press.
- DUNCUMB, P., and SHIELDS P. K., 1966, *The Electron Microprobe* (New York: John Wiley), pp. 284-95.
- HEINRICH, K. F. J., 1966, *The Electron Microprobe* (New York: John Wiley), pp. 296-377.
- HENKE, B. L., WHITE, R., and LUNDBERG, B., 1957, *J. Appl. Phys.*, **28**, 98-105.
- NICHOLSON, J. B., and HASLER, M. F., 1966, *Proc. 14th Ann. Conf. on Applications of X-ray Analysis, Denver, 1965* (New York: Plenum Press), pp. 720-9.
- OGIER, W. J., LUCAS, G. J., and PARK, R. J., 1964, *Appl. Phys. Letters*, **5**, 146-7.
- PHILIBERT J., 1963, *Proc. 3rd Int. Symp. on X-ray Optics and X-ray Microanalysis, Stanford, 1962* (New York: Academic Press), pp. 379-92.