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Quantitative Electron Probe Microanalysis of Carbon in Binary Carbides

II†—Data Reduction and Comparison of Programs

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The performances of four current matrix correction programs have been tested on a data file of measurements on 13 binary carbides between 4 and 30 kV. Both the metal lines as well as the carbon K α line have been measured, which resulted in 145 *k* ratios for the metals (relative to elemental standards) and 117 integral *k* ratios for carbon K α (relative to Fe₃C).

Evidence is presented that the existing sets of mass absorption coefficients for carbon K α radiation are perhaps not fully consistent and a new set is therefore proposed, which is in better agreement with the experimental results. Finally, it is shown that the modified Gaussian $\phi(\rho z)$ approach, when used in conjunction with the new set of mass absorption coefficients, leads to unexpectedly good results, with a relative root-mean-square value of 3.7%. This demonstrates that even for carbon very good accuracy can be obtained, provided that proper care is exercised in the measurements and the proper procedures are followed.

INTRODUCTION

In Part I we showed that for very light element x-radiation it is vital that the intensity measurements are performed in an integral fashion, in order to take into account the peak shape alterations due to differences in the chemical bond. We also showed that this tedious process can be considerably shortened once the so-called area/peak factors (APFs) (ratio between the integral and peak intensity ratios) are known. Further measurements can then simply be carried out on the peak again and multiplication with the appropriate APF will yield accurate integral intensity ratios. Here such measurements are described for 13 binary carbides at nine different accelerating voltages between 4 and 30 kV. The resulting data file can now be used in the final step in the quantification of light element analysis, i.e. the conversion of the measured *k* ratios into concentration units.

It was pointed out in Part I that two major problems are connected with this procedure. Firstly, no one knows which of the existing correction programs (if any) is capable of handling the very large correction factors which are necessary in the field of light elements. This is mainly due to the fact that until now there have been no data available to test them on. Also, there is a total lack of experimental $\phi(\rho z)$ data for light elements, for understandable reasons. In fact, attention has mainly been focused on the absorption correction. It is true that this correction is usually much larger than the atomic number correction for light elements. However, it has been demonstrated¹ that for light elements the differences in the atomic number corrections from program to

program can, in themselves, already account for the differences between calculated and nominal concentrations. Secondly, there are the mass absorption coefficients (MACs), which play an equally important role as the correction program itself. Unfortunately, the available sets²⁻⁷ of MACs for carbon show differences of 50–100%.

It is obvious, for both reasons, that it is impossible to make definite statements about the performance of any correction program as long as the MACs are not known with a precision of, say, 1%. For practical reasons it is very doubtful if such precise values will ever become available. For the time being we shall have to be content with statements on correction programs in conjunction with the specific set of MACs used. Of course, if a given program were known to be perfect, it would be possible to calculate the MACs backwards from the measured results. In any case, a large data file is necessary to test the results on.

There is one other way of assessing the published sets of MACs, through the use of the thin film model put forward by Duncumb and Melford.⁸ This model and its use will now be discussed.

THIN FILM MODEL

According to Duncumb and Melford,⁸ the necessary conditions for their thin film model are a high value of χ [$\equiv (\mu/\rho) \csc \psi$], in which μ/ρ is the MAC and ψ is the x-ray take-off angle, and a high overvoltage ratio E_0/E_c (E_0 is accelerating voltage and E_c the critical excitation voltage). These conditions are sometimes summarized in the requirement that $\chi \gg \sigma$, where σ is the Lenard coefficient, defined by $\sigma = 4.5 \times 10^5 / (E_0^{1.65} - E_c^{1.65})$. If ever the conditions for this model were to be satisfied, it would certainly be in

† For Part I, see p. 135.

the present case of carbon $K\alpha$ radiation at accelerating voltages above 30 keV.

Under these circumstances, the intensity of C $K\alpha$ radiation can be thought to originate only from a very thin film, very close to the surface of the specimen, and the intensity (I) can be written as

$$I: \phi(0)\Delta(\rho z)$$

in which $\phi(0)$ is the surface ionization and $\Delta(\rho z)$ is the thickness of the film (in units of mass depth), which, in turn can be considered to be inversely proportional to χ .

At very high overvoltages, the so-called 'limiting k ratio' can be expressed by

$$k = \frac{I_{MC}}{I_{Fe_3C}} = \frac{\phi(0)_{MC} \left(\frac{\mu}{\rho}\right)_{Fe_3C} X_{MC}}{\phi(0)_{Fe_3C} \left(\frac{\mu}{\rho}\right)_{MC} X_{Fe_3C}}$$

where I is the intensity of C $K\alpha$ radiation, M is the metal in the unknown carbide and X is the weight fraction of carbon. The values of $\phi(0)$ can be calculated, e.g., by using Love *et al.*'s expression.⁹

The useful thing about this model (if it applies) is that it predicts a limiting k ratio which is independent of the take-off angle and that it allows the relationships between the MACs in the standard and the specimen to be tested. Part of the present work has been devoted to such a test.

EXPERIMENTAL

In order to improve the statistics and to overcome the problems connected with slight inhomogeneities, inevitably present in most carbides, an extended series of peak k ratio measurements were carried out for carbon and for the metals involved. The measurements were performed at 4, 6, 8, 10, 12, 15, 20, 25 and 30 keV. In order to avoid excessive dead-time corrections for the metal lines (see Part I), the metals and carbon were measured separately.

The procedure for the metals was as follows. In a preliminary survey, 6–10 suitable areas for analysis were located, the coordinates of which were stored in a points table in the computer. In the actual measurements the computer was instructed to move the specimen in five steps in a certain direction in each of these areas and to take point counts at each interval. In total 30–50 measurements were thus performed for each carbide at each of the nine potentials. The beam current was usually adjusted as to ensure a maximum count rate of 2500 counts s^{-1} , in order to avoid dead-time problems. Where possible (Ta and W), both M and L lines were measured. The air-jet was not used in this case.

In this way 145 accurate k ratios were accumulated. To give some idea about the homogeneity of the specimens, it can be stated that the differences between the maximum and minimum count rates very rarely exceeded 3%. The standard deviation was usually better than 1%. The background was

measured in the usual way, i.e. on either side of the peak, and interpolated.

For carbon a similar procedure was followed. In this case the air-jet was, of course, used and the number of measurements was increased to ten areas each with five measurements. Also, a waiting period of 30 s was programmed with the beam switched on (see Part I) for accelerating voltages higher than 6 kV and a 1-min period for lower potentials before the measurements were started.

Measurements on B_4C , SiC, TiC and VC (and Fe_3C as a standard) were performed with the same (relatively wide) pulse-height analyser (PHA) settings of 0.6 V for the threshold and 5 V for the window. The window was narrowed to 2 V and the threshold increased to 1 V for the chromium carbides and the carbides of elements of the 5th and 6th Periods, in order to prevent interferences as much as possible. Typical beam currents were between 100 and 300 nA and the variations between extremes in count rates were usually within 6%. The variations in the position of the carbon peak were accounted for by a repeated, very slow peak search procedure, which the automation program was instructed to carry out between measurements on standards and specimens.

Special attention was paid to the correct determination of the background. This was measured at the position of the carbon peak on each of the constituent elements. That of carbon was obtained by interpolation vs atomic number between the values for boron and silicon. Subsequently, the background was composed on the basis of the weight fractions of the constituent elements and subtracted from the gross intensities. The final k ratios obtained with this procedure differed only slightly (maximum 3%) from those obtained by a straightforward interpolation between either side of the peak. This is because the former procedure affects both the standard and the specimen and much of the effects are lost in taking the ratio. Besides, the peak-to-background ratio for many carbides is high. Nevertheless, the former procedure certainly deserves preference and is probably the only correct one. The second procedure can result in dramatic errors (several hundred percent) for carbon concentrations much below 1%.

In total 117 accurate peak k ratios with respect to Fe_3C were accumulated, which served, after multiplication with the proper APF, as the data file on which the various correction programs could be tested. All numerical data have been given in an internal report.¹⁰

RESULTS

Peak K ratios for metals and carbon

Figures 1 and 2 show some of the results of these measurements. They are typical examples in the sense that the k ratio for carbon in systems with a stronger absorption than in the Fe_3C standard (e.g. Mo_2C) shows an initial decrease, followed by a kind of saturation, which is followed in turn by an increase

Figure 1. Peak k ratios for vanadium $K\alpha$ (pure elemental standard) and carbon $K\alpha$ (Fe_3C standard) as a function of accelerating voltage. H, R and B refer to the limiting k ratio calculated on the basis of mass absorption coefficients according to Henke *et al.*,⁷ Ruste² (partially modified set of Henke and Ebisu⁶) or this work, respectively. Note the large differences in scale between the metal and carbon k ratios.

again. The reverse is found in cases with a lower absorption than in the standard (e.g. VC).

Apparently it is too simple to expect the limiting k ratio to attain a simple saturation level. In fact, if our measurements were not pursued up to 30 keV we would easily have been misled by the saturation, frequently observed between 10 and 20 keV, with the result that the observed limiting k ratios would be assumed to take completely wrong values. These effects are, of course, directly connected with the ways in which the relative intensities in the various carbides vary with potential.¹⁰

If the measured k ratios for carbon are extrapolated to ca 35 keV, it becomes apparent that the existing sets of MACs are not fully consistent and do not lead

to good agreement between observed and predicted limiting k ratios. Table 1 gives a survey of the extrapolated values. These observations have partially been the reason for us to propose a new and consistent set of MACs, which provide better agreement, as Table 1 shows. The new set is given in Table 2, together with the sets of Ruste,² Henke and Ebisu⁶ and Henke *et al.*⁷ We shall return to this point later.

One final remark on the measurements must still be made, namely that the measurements at 4 kV were sometimes difficult to reproduce. This is undoubtedly the result of the fact that at these low potentials x-ray generation only takes place in an extremely superficial layer; calculated $\phi(\rho z)$ curves show that for many

Figure 2. Peak k ratios for molybdenum $L\alpha$ (pure elemental standard) and carbon $K\alpha$ (Fe_3C standard) as a function of accelerating voltage.

Table 1. Extrapolated peak k ratio for carbon $K\alpha$ radiation, relative to Fe_3C , compared with the limiting k ratio predicted on the basis of different sets of mass absorption coefficients

Compound	Observed k ratio	Calculated k ratio according to different MACs		
		Ruste ^{2a}	Henke <i>et al.</i> ⁷	This work
B ₄ C	0.69	0.87	0.90	0.79
SiC	1.90	2.06	2.16	2.09
TiC	5.70	6.39	6.68	5.63
VC	4.20	4.76	4.97	4.25
Cr ₂₃ C ₆	1.35	1.30	1.36	1.28
Cr ₇ C ₃	2.15	2.12	2.22	2.08
Cr ₃ C ₂	3.18	3.11	3.24	3.05
ZrC	1.18	0.85	1.28	1.12
NbC	1.15	1.00	1.30	1.06
Mo ₂ C	0.82	0.96	0.95	0.79
TaC	1.17	0.74	0.83	0.97
WC	1.05	0.69	0.83	0.93
W ₂ C	0.52	0.32	0.38	0.42

^a Partially modified set of Henke and Ebisu.⁶

carbides at 10 kV the ultimate depth from which generated x-rays may reach the surface is already below 0.25 μm . Hence, the system is then extremely vulnerable to all kinds of surface effects, such as artefacts introduced by polishing and cleaning procedures, surface relief, etc. We would, therefore, not advise carbon measurements to be performed at potentials much below 10 kV; instead, we prefer the region below 8 and 12 kV, especially as most metal lines can be excited satisfactorily in this range.

Comparison of correction programs

Four current correction programs were tested on the extensive data collected in this work. The first program was the ZAF program supplied by Tracor

Table 2. Mass absorption coefficients for carbon $K\alpha$ radiation according to various sources

Absorber	MAC			
	Henke and Ebisu ⁶	Ruste ²	Henke <i>et al.</i> ⁷	This work
B	37020	37020	37000	41000
C	2373	2373	2350	2373
Si	36980	36980	36800	37000
Ti	8094	8094	8090	9400
V	8840	9236	8840	10100
Cr	10590	10482	10600	10950
Fe	13300	13300	13900	13500
Zr	31130	31130	21600	24000
Nb	33990 ^a	24203	19400	23200
Mo	32420 ^a	15500	16400	19200
Ta	18390	20000	18400	16000
W	18750	21580	18800	17000

^a Extrapolated over absorption edge.

Northern, henceforth referred to as ZAF. Details of this program can be found in Ref. 1. The second program was that of Love and co-workers (LOS),^{11,12} the third that by Ruste² and the fourth our own program, BAS.^{1,13}

The usual approach for testing a program on a data file is that for a given concentration in the file the intensity ratio, k' , is calculated and compared with the actually measured k ratio. This means that the program is, in fact, run backwards. The k'/k values are usually displayed in a histogram, showing the number of analyses as a function of k'/k and the shape of the histogram, together with the root-mean-square (r.m.s.) deviation are used as a final judgement of success.

Metal Analyses. The results of the four programs for the 145 metal k ratios are represented graphically in Fig. 3. The averages and r.m.s. values are given in Table 3. As it turns out, the ZAF program seems to be the most satisfactory for this particular type of file; particular in the sense that in most cases only a very small atomic number correction (smaller than 5%) is necessary. It seems that the application of a different expression for the ionization potential in the Ruste program leads to a slight deterioration in the results. The LOS and BAS programs lead to comparable results. It is remarkable, though that in the LOS program a small bias can be noticed, which is similar to that observed earlier,¹ when the four programs were compared on a test file containing 441 analyses

Figure 3. Histograms showing the results of four correction programs for 145 metal analyses between 4 and 30 kV; k' is the calculated and k the measured k ratio.

Table 3. Root-mean-square deviations and averages obtained with four correction programs for 145 metal analyses between 4 and 30 kV

Program	Average	R.m.s. (%)
ZAF	0.9989	1.4
RUSTE	0.9934	1.5
LOS	0.9948	2.0
BAS	1.0014	2.1

of a widely varying nature. Moreover, it is interesting that the figure of merit in the present case is in the reverse order when compared with earlier¹ tests on the atomic number correction. This may serve as an example that it can be very difficult to make firm statements on the performance of correction programs, especially if the test file is of a specific nature.

As far as the BAS program is concerned, it must be remarked that the present file contains a relatively large number of analyses at low overvoltage ratios. It has been stated before^{1,13} that this program is more sensitive to low overvoltage ratios than others; better results would have been obtained if only analyses at overvoltages exceeding 1.5 had been performed.

Carbon analyses. It is more difficult to assess the performance of the programs for carbon analyses, mainly for two reasons.

Firstly, the carbon measurements were carried out with respect to a complex standard (Fe_3C), and this may obscure to a certain extent any malfunctioning of a particular program as the calculations proceed through the primary calculation of a correction factor (k ratio of Fe_3C relative to an imaginary carbon standard). The measured k ratio of a carbide, relative to Fe_3C , is then multiplied by this factor, after which the program converts the resulting k ratio into concentration. One could argue that in such a procedure one does not have to rely so heavily on the proper functioning of the program. Hence it is perfectly conceivable that both in the carbide and in the standard appreciable errors might be made; yet the final result could turn out to be acceptable as these errors might well be divided out in taking the ratio.

Secondly, a further complicating factor is, again, the uncertainty in the MACs. This effect is noticeable in two ways: first it renders the absorption in the carbide uncertain, second in a way that the absorption coefficient of C $K\alpha$ in iron plays a major role, as this comes in through the calculation of the correction factor for Fe_3C and is, therefore, implicitly contained in all k ratios.

For both reasons it was considered vital to measure the (area) k ratio of C $K\alpha$ in Fe_3C relative to glassy carbon as a standard, in order to check the performance of the programs in this crucial first step. The results are shown in Fig. 4. The k ratios, calculated by the BAS program, agree perfectly with the measured values between 4 and 12–15 kV. In this case our own MACs were used; inspection of Table 2

Figure 4. Measured area k ratio for carbon $K\alpha$ in Fe_3C relative to glassy carbon, as compared with the results calculated by the BAS program.

shows, however, that the differences between the various sets can safely be neglected for carbon and iron.

Above 15 kV increasingly low values are calculated, which must be attributed to the program's failure to predict any longer the proper $\phi(\rho z)$ curves in carbon at such high overvoltage ratios. Apparently a better parameterization is necessary for these extreme conditions. The good agreement between 4 and 15 kV can be interpreted in that all carbides could just as well have been measured relative to glassy carbon.

The Ruste program is second best in this range, giving about 5% too low values, followed by the LOS program, with up to 10% too high values. The ZAF program was the least satisfactory, with 6% too low values at up to 8 kV, 8–10% too high values between 8 and 15 kV, good results at 20 kV and suddenly 18% too low again at higher potentials. Above 15 kV the LOS program is best, followed by the Ruste, BAS and ZAF programs.

After this very important first step, final calculations were carried out using the sets of MACs in Table 2. The results are given in Tables 4 and 5.

A few things should be noted in Tables 4 and 5. It is apparent that Henke *et al.*'s⁷ newest set of MACs give significant improvements in the r.m.s. values for all

Table 4. Root-mean-square values (%)^a for various programs using different sets of mass absorption coefficients^b

Program	MAC		
	Ruste ²	Henke <i>et al.</i> ⁷	This work
BAS	16.78	10.85	3.69
LOS	14.19	11.33	8.98
RUSTE	12.56	10.65	11.94
ZAF	19.40	15.27	17.86

^a These apply to the ratio between the calculated and nominal concentration for a measured k ratio.

^b The data file contains 117 carbon analyses between 4 and 30 kV in 13 binary carbides.

Table 5. Averages obtained for various programs, using different sets of mass absorption coefficients

Program	Ruste ²	Henke <i>et al.</i> ⁷	This work
BAS	1.045	0.942	0.988
LOS	1.009	0.914	0.958
RUSTE	0.991	0.894	0.946
ZAF	1.042	0.929	0.989

programs involved, although all programs have averages that are too low with this set, which might indicate that their values are generally on the low side. The use of our new set gives further improvements for the BAS program as well as for the LOS program. At the same time, the averages are brought closer to unity again for all programs.

The use of our set, together with our program, gives almost spectacular results, as Fig. 5 shows. The individual values in our set are intermediate between Ruste's² and Henke *et al.*'s⁷ but in general are closer to Henke *et al.*'s newest values; they do not deviate by more than 20% from Henke *et al.*'s values.

Justification for new set of mass absorption coefficients

There have been a number of considerations that brought us to introduce a new set of MACs. We realize, of course, that none of them gives full proof of the correctness of the values proposed. However, together they might be considered as circumstantial evidence.

We have already seen (Table 1) that the limiting k ratios for carbon, calculated by the thin film model, agree better with the measured values when using our new set. Further, in most cases, the calculated concentrations vs accelerating voltage show more or less horizontal lines,^{10,14} which merely shift up and

down with variation in the chosen MAC. Figures 6 and 7 show two examples of calculations. The application of our new values brings the line almost on the nominal composition. The next reason is one of consistency: we have seen already that our program works perfectly (up to 15 kV) for carbon in iron (Fig. 4); this being the case, it would be expected to do likewise for the three chromium carbides, because all equations used in the program are in some way or another functions of atomic number and atomic weight, and chromium and iron are very close in the Periodic system. As it turns out, the results are indeed very good in this case, regardless of which MACs are used. Moving one step back in the Periodic system brings us to vanadium, in which case suddenly 10–12% too low concentrations are calculated with Henke *et al.*'s⁷ values. Such an observation might point to an inconsistency in the MACs. For titanium even larger deviations are found, which is surprising as the systems Ti–C and V–C require the least correction of all binary carbides investigated. Similar reasoning can be applied to the sequence ZrC, NbC and Mo₂C: NbC comes out very well with Ruste's² MACs whereas ZrC comes out much too high and Mo₂C too low. In this case it would be understandable because the wavelength of C K α is very close to the M5 absorption edge of these metals and the MACs have to be determined in a strongly curved region of the MAC vs wavelength plot for these metals. This is not the case for Ti and V, however; it can only be remarked that the values reported by Henke *et al.*⁷ are still the same as those by Henke and Ebisu.⁶ Apparently no evidence for revised values has been obtained since then.

A complete survey of our new set of MACs, as compared with the other sets, is shown in Fig. 8. It is interesting that our values for Ta and W have a tendency to take away much of the discontinuity in Henke *et al.*'s⁷ values and perhaps provide a better connection with the atomic numbers beyond 76.

Figure 5. Histogram showing the results obtained with the BAS program for 117 carbon analyses between 4 and 30 kV when the new set of mass absorption coefficients are used. Note that the number of analyses is displayed vs the ratio between calculated (c') and nominal concentration (c).

Figure 6. Results obtained with the BAS program for carbon analysis in VC, using three sets of mass absorption coefficients: H = Henke *et al.*,⁷ R = Ruste,² B = this work.

Figure 7. Results obtained with the BAS program for carbon analysis in Mo_2C , using three sets of mass absorption coefficients: H = Henke *et al.*,⁷ R = Ruste,² B = this work.

Likewise, the values for Ti and V seem, to some extent, to fill up a dip in Henke *et al.*'s⁷ values.

At present the new set can only be regarded as a convenient and consistent set to go with our program in its present state. As we have pointed out before, it is still possible that the introduction of new MACs is necessary to mask inadequacies in the correction program, e.g. in the atomic number correction or in the shape of the $\phi(\rho z)$ curves. As long as there is considerable uncertainty about both the functioning of the program and the correctness of the MACs there is little use in trying to improve either of them. Only if more certainty about the MACs could be obtained

would it perhaps be necessary to improve the program or vice versa. In either case the data file presented in this work would be very useful for either procedure.

At present work is in progress on similar measurements for boron and nitrogen and the results will be reported later.

Summarizing the results, we can state that quantitative electron probe microanalysis of carbon is possible with very good accuracy, provided that the intensities are measured in an integral fashion, proper care is exercised in the measurements and a suitable correction program and a consistent set of mass absorption coefficients are used.

Figure 8. Variation of the mass absorption coefficients for carbon $K\alpha$ radiation with atomic number of the absorber. Values of three sources are compared: H = Henke *et al.*,⁷ R = Ruste,² B = this work.

REFERENCES

1. G. F. Bastin, H. J. M. Heijligers and F. J. J. van Loo, *Scanning* **6**, 58 (1984).
2. J. Ruste, *J. Microsc. Spectrosc. Electron.* **4**, 123 (1979).
3. W. Weisweiler, *Mikrochim. Acta* **11**, 179 (1975).
4. E. Kohlhaas and F. Scheiding, *Arch. Eisenhüttenwes.* **41**, 97 (1970).
5. D. Fornwalt and A. Manzione, *Norelco Rep.* **13**, 39 (1966).
6. B. L. Henke and E. S. Ebsu, *Adv. X-Ray Anal.* **17**, 150 (1974).
7. B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro and B. K. Fujikawa, *At. Data Nucl. Data Tables* **27**, 1 (1982).
8. P. Duncumb and D. A. Melford, in *4th International Conference on X-Ray Optics and Microanalysis*, edited by R. Castaing, p. 20. Hermann, Paris (1966).
9. G. Love, M. G. Cox and V. D. Scott, *J. Phys. D* **11**, 23 (1978).
10. G. F. Bastin and H. J. M. Heijligers, *Quantitative Electron Probe Microanalysis of Carbon in Binary Carbides*, Internal Report, University of Technology, Eindhoven (1984).
11. G. Love, M. G. Cox and V. D. Scott, *J. Phys. D* **11**, 7 (1978).
12. G. Love and V. D. Scott, *J. Phys. D* **11**, 1369 (1978).
13. G. F. Bastin, F. J. J. van Loo and H. J. M. Heijligers, *X-Ray Spectrom.* **13**, 91 (1984).
14. G. F. Bastin and H. J. M. Heijligers, in *Microbeam Analysis*, edited by A. D. Romig, Jr. and J. I. Goldstein, p. 291. San Francisco Press, San Francisco (1984).