

Quantitative electron probe microanalysis of nitrogen

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Original Papers

Quantitative Electron Probe Microanalysis of Nitrogen

G. F. BASTIN, H. J. M. HEIJLIGERS

Laboratory for Solid State Chemistry and Materials Science, University of Technology, Eindhoven, The Netherlands

Summary: Quantitative electron probe microanalysis of nitrogen has been performed on 18 nitride specimens in the voltage range of 4–30 kV. A conventional lead stearate and a new W/Si multilayer analyzer crystal (2d = 5.98 nm) were used simultaneously. The net peak count rates on the latter crystal were approximately 2.8 times higher than on the lead stearate crystal. In addition, significant improvements in the peak to background ratios were achieved, which proved critical when dealing with difficult nitrides such as ZrN, Nb₂N, and Mo₂N. A most conspicuous feature of the new crystal, however, is its effective suppression of higher-order reflections in the wavelength range of N-K α . As a result, backgrounds are free of interfering lines and spectral artifacts, which facilitates accurate background determination. Two procedures for the analysis of nitrogen in the presence of titanium are also discussed. One procedure is based on the assumption that the area-peak factor (APF, integral k-ratio/peak k-ratio) of the N-K α peak in Ti–N compounds relative to a nitrogen standard (Cr₂N) has a fixed value which can be used in order to separate the Ti- β peak from the N-K α peak. Extensive tests on a number of compositions in the Ti–N system have shown that it is possible to do quantitative analysis of nitrogen in Ti–N compounds with a relative accuracy of better than 5%. For very low levels of nitrogen (below 15 at%) the APF method was found unsuitable. In such cases, however, the well-known multiple least-squares digital-fitting techniques appeared to do an excellent job. In order to account for the effects of peak shape alterations in the N-K α peak, all nitrogen spectra were recorded in integral fashion and compared with those of the Cr₂N

standard. The shape alterations for the N-K α peak were much smaller than for B-K α and C-K α radiations: The observed values for the area-peak factor relative to Cr₂N differed less than 5% from unity. The present work has resulted in a database containing 144 integral k-ratios for N-K α and 149 peak k-ratios for the x-ray lines of the metal partners in the nitrides. Our own Gaussian $\phi(\rho z)$ matrix correction procedure “PROZA,” used in conjunction with a set of improved mass absorption coefficients, yielded excellent results for the nitrogen data: An average value of $k_{\text{calc}}/K_{\text{meas}}$ of 1.0051 and a relative root mean square deviation of 3.99%.

Introduction

Presented here is part of a series of systematic investigations into the feasibility of quantitative electron probe microanalysis of the ultralight elements B, C, N, and O. This research program was initiated in 1983 and now is successfully completed. The results for the elements carbon (Bastin and Heijligers 1984, 1986a) and boron (Bastin and Heijligers 1986b,c) have been published in detail.

The primary object of our research efforts in the field of ultralight element analysis has always been the collection of reliable measurements on well-characterized specimens over a wide range of experimental conditions. This has been done with a twofold purpose: On the one hand, such databases are invaluable for assessing the performances of existing and future bulk matrix correction programs and certainly in efforts to improve them. On the other hand, this assessment and optimization can only be done in conjunction with correct mass absorption coefficients (MACs) for the light element radiations and these MACs are not always available with the required precision of let us say 1%. It is inevitable, therefore, that the optimization process is iterative in nature: Any improvement in a specific program will go unnoticed when incorrect and inconsistent MACs are used and vice versa. Using our databases, better and more consistent sets of MACs can be expected.

Address for reprints:

G. F. Bastin
Laboratory for Solid State Chemistry and Materials Science
University of Technology
P.O. Box 513
NL-5600 MB
Eindhoven, The Netherlands

As we have pointed out on several occasions (e.g., Bastin and Heijligers 1990), quantitative EPMA of ultralight elements is not only a matter of using good matrix correction procedures and MACs; items such as specimen preparation and correct experimental procedures are of at least equal importance. Contamination effects with carbon, but certainly also with oxygen (Bastin and Heijligers 1988a) can have a disastrous effect on the measurements due to the time-consuming nature of the latter. Likewise, a lack of electrical conductivity of the specimen can have an awkward effect on a measurement (Bastin and Heijligers 1988b). By far the most prominent problems in the intensity measurements, however, are the sometimes extreme alterations in the shapes of the x-ray emission peaks of ultralight element radiations from one compound to another. Contrary to the well-known associated effects of peak shifts, it is not so easy to deal with peak shape alterations in a wavelength-dispersive analyzer. In such a system, correct intensity measurement requires, in principle, the full integral recording of the peaks in the specimen and the standard; a very time-consuming procedure. We have demonstrated (Bastin and Heijligers 1986a,c) that there is a fixed ratio between the correct integral (or area) k-ratio and the usually incorrect but easy to measure peak k-ratio, and we have introduced the term area/peak factor (APF) for this ratio. In cases where repeated measurements in the same system are required, it can be advantageous to establish the value of the APF for the compound in question only once, relative to the selected standard from integral recordings of the peaks. Any further measurements, even at different accelerating voltages, can then be carried out on the peak again and the peak k-ratios can easily be converted into meaningful integral k-ratios by simple multiplication with the APF.

In the sequence of the ultralight elements B, C, N, and O, nitrogen is definitely the most difficult element to deal with because of the exceptionally low count rates usually observed for N-K α radiation. This is caused by the N-K α wavelength falling into the carbon K absorption edge, and carbon is abundantly present in the detection system (conventional lead-stearate crystal, polypropylene detector window). As a result, count rates for N-K α on a lead-stearate crystal can be an order of magnitude lower than even B-K α and C-K α . Fortunately, newer synthetic multilayer crystals can bring significant improvements here in more than one respect. Besides providing much higher peak count rates, they can also suppress higher-order reflections from metal lines which frequently interfere with the light element radiation itself. These interferences are a major nuisance in light element analysis and are all the more bothersome when count rates decrease to very low levels.

All things considered, it was expected that the present work on nitrogen would be the most difficult and time-consuming project in the series of investigations carried out so far.

Experimental

For the purpose of the present work, it is essential to have fully homogeneous nitride specimens of 100% density and accurately known compositions. Because it was virtually impossible to obtain such specimens commercially, we were forced to prepare them in our own laboratory. Only 5 of 18 nitride specimens were obtained from external sources:

Hexagonal BN, produced by Chemical Vapour Deposition, kindly supplied to us by Mr. G. Verspui, C.F.T. Philips, Eindhoven, The Netherlands.

Cubic BN (powder, particle size up to several tens of μm , produced by the "Borozon" process), kindly supplied to us by Mr. R.C. de Vries, General Electric Co., Schenectady, NY.

Si₃N₄, produced by CVD techniques on a Si substrate, layer thicknesses of 1 and 2.5 μm , respectively. These specimens were supplied to us by Mr. P. v.d. Straten, formerly with C.F.T., Philips, Eindhoven, The Netherlands.

TiN, produced by CVD techniques on a Ti substrate, in ± 5 successive steps to yield layer thicknesses up to 2 mm. This specimen was also supplied to us by Mr. G. Verspui.

Fe₄N, produced by low-temperature (560°C) nitriding of Fe, resulting in a ± 20 μm thick nitride layer. This specimen was kindly supplied to us by Ir. D. Schalkoord, University of Technology, Delft, The Netherlands.

Preparation of Nitrides

The preparation of massive, homogeneous nitride specimens turned out to be a major task. In the majority of cases the so-called "reactive arc-melting" technique has been used in which the metal components were melted in a conventional arc-melting equipment (Tungsten electrode, water-cooled copper hearth) under Argon-Nitrogen mixtures (10 cm argon, 20 cm nitrogen). In general, this technique led to the production of two-phased alloys: α -Me(N) (solid solution) + MeN for the metals Ti, Zr, and Hf; or Me(N) + Me₂N for V, Cr, Nb, and Ta. Subsequent annealing of these starting materials at temperatures between 1100 and 2000°C during 12–140 h in a 6 kW RF furnace under purified nitrogen usually yielded homogeneous massive specimens of TiN, VN, ZrN, and HfN.

Similar procedures for Cr and Ta led to the formation of the subnitrides Cr₂N and Ta₂N, while in the case of Nb the Nb₄N₃ phase was obtained. Compounds like Ti₂N, V₂N and Nb₂N could not be produced in the form of monolithic specimens. In these cases diffusion layers

could be grown by heating the elements in pure nitrogen at elevated temperatures. Areas close to the $\text{Me}_2\text{N}/\text{MeN}$ (or Me_4N_3 in the case of Nb) interface were selected and marked by microhardness indentations. The compound TaN could be made by heating a massive Ta_2N specimen in nitrogen at temperatures between 1000 and 1200°C, leading to a $\pm 10 \mu\text{m}$ thick TaN layer. Extremely difficult to produce were the compounds CrN and Mo_2N . The former could be made by low-temperature (900°C) nitriding of a RAM-melted specimen in NH_3 , leading to the formation of $\pm 10 \mu\text{m}$ thick CrN layers very locally; usually in cracks and crevices only. Mo_2N specimens were made by nitriding Mo sheets at 900°C in NH_3 during 100 h. This procedure yielded a $\pm 30 \mu\text{m}$ thick Mo_2N layer. In general these procedures turned out to be rather tricky and difficult to reproduce.

Sufficiently thick ($\pm 30 \mu\text{m}$) AlN layers finally were produced by CVD techniques on a graphite substrate, using Al shavings and HCl gas, in order to produce gaseous AlCl_3 , which was then mixed with NH_3 gas and passed over a heated graphite substrate. More specific details on the production routes used in the preparation of our nitrides can be found in an internal report (Bastin and Heijligers 1988c).

Characterization of Nitride Specimens

The compound Cr_2N was selected as the nitrogen standard throughout this work because: (a) no spectral interferences are produced in the relevant wavelength range and (b) it can relatively easily be produced in reasonable quantities. Because appreciable amounts of Cr_2N were needed, two batches have been prepared and much care has been exercised in finding the correct composition. Both batches were prepared from RAM-melted starting materials which were further annealed under nitrogen at elevated temperatures. They were carefully checked for homogeneity with the electron probe microanalyzer prior to subjection to chemical analysis. Thanks are due to Dr. P. Karduck of the University of Technology in Aachen, FRG for supplying these chemical analyses. The first batch was prepared by annealing at 1000°C during 91 h; the second at 1400°C during 90 h. The results of the chemical analyses for Batch 1 which was used in this work are given in Table I. The data obtained were carefully checked against the EPMA analyses of Cr and, most important of all, the most recent material on the phase diagram Cr–N currently available (Holleck 1984).

According to this diagram, the homogeneity range of Cr_2N extends from 30 to 33 at %N at 500°C while at higher temperatures both limits shift toward lower N contents. This is in good agreement with the results of the chemical analyses: For the specimen produced at 1000°C (Batch 1), a combined N+O content of 31.73 at% was reported, whereas at the higher temperature of 1400°C, a correspondingly lower combined N+O content

should be expected and this was indeed found (29.91 at%).

Unfortunately, significant problems were encountered in the analysis of the more “difficult” nitrides (TiN, ZrN, and HfN). For a number of reasons we were, in these cases, forced to use a different approach in order to find the “most probable composition” of each of the nitride specimens. This approach was based on a process of achieving the maximum degree of consistency in the results. In this process use was made of every single bit of information that we could lay our hands on: the information on phase diagrams, results of the microprobe analyses of the metals in the nitrides, results of the nitrogen analyses themselves, consistency in the variation of the mass absorption coefficients (B, C, N, O radiations) in each of the metals, known biases (from earlier work on B and C) of existing correction programs in specific cases, our own experience in solid-state chemistry and materials science, thermodynamic considerations, ad infinitum. Some features, for example, the typical deep golden color (TiN, ZrN, and HfN) can be a good and very sensitive indication for approaching the stoichiometric composition.

In view of all the uncertainties involved, the process of establishing the most probable compositions can be only iterative in nature. Nevertheless, we finally succeeded in finding a set of compositions giving the desired degree of consistency, and we sincerely believe that this set is very close to the truth. Table II gives a survey of these compositions.

Mounting, Polishing, and Examination Procedures

Each of the nitride specimens, small pieces of the Cr_2N standard (Batch 1), and pieces of the pure metals were mounted and polished separately in order to avoid problems in polishing materials exhibiting extreme differences in hardness. The specimens were mounted in copper-filled resin and very carefully polished. Diamond abrasive disks were used for the coarse stages (70, 30, and 15 μm grain size) of polishing; final polishing was done on a Nylon cloth with diamond paste (6, 3, and 1 μm). Once a satisfactory polish was obtained, the

TABLE I Chemical analyses of the Cr_2N specimen (Batch 1) used as the nitrogen standard throughout this work

	N-content wt%	O-content wt%	Cr-content wt%
	10.5	0.49	89.01
	10.8	0.50	88.70
	10.6	0.46	88.94
	11.2	0.52	88.28
	10.4	0.43	89.17
Aver.	10.7 (wt%)	0.48 (wt%)	88.82 (wt%)
	30.53 (at%)	1.20 (at%)	68.27 (at%)

TABLE II Compositions of the nitride specimens used in the present investigation (wt%)

Compound	N-content	O-content	Metal content
BN (Hex)	56.45	—	43.55
(Cub)	56.45	—	43.55
AlN	34.18	—	65.82
Si ₃ N ₄	39.24	0.70	60.06
Ti ₂ N	11.84	—	88.16
TiN	22.50	—	77.50
V ₂ N	11.99	0.78	87.23
VN	16.04	0.31	83.65
Cr ₂ N (1)	10.70	0.48	88.82
(2)	10.10	0.24	89.66
CrN	21.22	—	78.78
Fe ₄ N	5.60	—	94.40
ZrN	12.70	0.67	86.63
Nb ₂ N	6.55	0.46	92.99
Nb ₄ N ₃	9.79	0.72	89.49
Mo ₂ N	5.80	—	94.20
HfN	6.06	0.29	Hf 91.36 Zr 2.29
Ta ₂ N	3.47	0.24	96.29
TaN	6.51	0.22	93.27

specimens were cut out again in small cubes of mounting resin containing the specimen after which all edges of the polished face were carefully rounded off. Next the specimens were turned upside down onto the bottom of a freshly polished mould to be remounted groupwise: the Cr₂N standard in the centre and specimens such as TiN, Ti₂N, and Ta grouped around the standard. This procedure was found to guarantee perfectly plane and parallel top and bottom planes of the new mount, which is extremely important in view of the correctness of the take-off angle in light-element work. Superficial contaminants were removed by a brief polishing treatment on a soft cloth using 0.05 μm γ -Alumina. Final cleaning was done ultrasonically using alcohol.

Optical microscopy was used to get a first impression of the quality of the specimens as far as the presence of second (or third) phases, presence of unreacted starting materials, grain size (using polarized light), etc. are concerned.

In some cases (BN, Cr₂N, Mo₂N) standard x-ray diffraction procedures were used to identify the compounds. Microprobe analysis of the metal component as well as of the N and O content was used to check vital items, i.e., homogeneity, identity of second phases and, sometimes, the compositions of the specimens. Special attention was paid to the consistency of the results obtained in those cases where more than one compound in a particular system was available (Ti, V, Cr, Nb, Ta). This is, by the way, the reason why whenever possible we try to have more than one compound in the same binary system at our disposal. All the examination procedures mentioned here have played a more or less

important role in the complicated process aimed at finding the most probable compositions.

Technical Details of the Microprobe Used

All our measurements were performed on an automated JEOL Superprobe 733, equipped with four wavelength-dispersive spectrometers and an energy-dispersive system (TRACOR Northern TN-2000). The automation system was also supplied by TRACOR Northern (TN-1310).

The first spectrometer, specifically designed for light(er) elements, was equipped with a conventional lead-stearate crystal (2d spacing ± 100 Å) for the analysis of B, C, N, and O, and a TAP crystal for higher Z elements. The specially purchased fourth spectrometer was equipped with two new synthetic multilayer crystals. The first one was a W/Si multilayer (200 pairs of layers, 2d spacing 5.98 nm), eminently suited for the analysis of (C), N, O, and F. The second one was a Mo/B₄C multilayer (2d spacing 14.48 nm), optimized for the analysis of B and Be. Both crystals were supplied by Ovonic Synthetic Materials Corporation, Troy, MI. The other two spectrometers each contained conventional LiF and PET crystals. Proportional counters were used in all detection systems: in spectrometers 1 and 4 the gas-flow type (Argon-10% Methane); in spectrometers 2 and 3 the sealed Xenon type.

On previous occasions (Bastin and Heijligers 1984, 1986a), we have discussed the tests on the operating conditions of the microprobe, such as the correctness of the accelerating voltage, stability of the beam current and beam position, etc., which all were found highly satisfactory. Our instrument is equipped with an automated beam current detector and count rates are automatically corrected for any drift that might occur during the measurements.

All nitrogen measurements were carried out with the lead-stearate (STE) and W/Si multilayer (LDE) crystals simultaneously under identical conditions. This enabled us in the first place to compare the performances of both crystals in a quite straightforward way. Initially, we used an air jet (Bastin and Heijligers 1984, 1986a) in order to prevent build-up of carbon under the electron beam which could produce a drastic reduction in nitrogen count rates with time as a result of the strong absorption of N-K α x-rays in carbon. Gradually it became clear, however, that certain sensitive nitrides such as ZrN, HfN, and TaN can be oxidized at an incredibly fast rate under electron bombardment (Bastin and Heijligers 1988a,c), leading to a rapid decrease of the N-K α signal with time. Measurements on these materials were, therefore, repeated without the use of the air jet. The conventional oil-diffusion pump used in our previous work (Bastin and Heijligers 1984, 1986a) has been replaced by a turbomolecular pump in an effort to remove one of the main sources of hydrocarbons in the vacuum system.

Measurements of Area-Peak Factors

The area-peak factors (APFs) for N-K α radiation were determined from integral recordings of the N-K α peaks emitted by standard and specimens. The spectrometers (1 and 4) were hereby scanned stepwise over the range of approximately 2.8–3.5 nm. For the multilayer crystal (LDE) this corresponded to the linear range of 130–165 mm in steps of 0.07 mm (1.495×10^{-3} nm). For the stearate crystal (STE) the range was 79–99 mm in steps of 0.04 mm (1.426×10^{-3} nm). In each interval, counts were accumulated during 10 s and subsequently the numbers were transferred to successive channels of the multichannel analyzer and displayed on the screen of the CRT of the EDX system. After completion of the spectra they were stored on diskette. The beam current was measured before and after the measurement and these values were also stored with the spectra. A typical sequence in the measurement of, e.g., CrN would be: Start on Cr₂N (nitrogen standard), followed by three successive measurements on CrN, after which a spectrum on pure Cr would be recorded. Then the complete cycle would be repeated once more. The vast majority of APF measurements were carried out at 10 kV and a beam current of 300 nA. The pulse height analyzer conditions (Ortec electronics) were chosen such as to produce a N-K α pulse at 2.0 V (Counter high tension 1700 V). The threshold was usually fixed at 1.0 V and a window of 2.0 V was commonly used.

The stored spectra were processed in order to obtain the net integral (area) and peak intensities from standard and specimen. The first step in this process was to subtract the background and this turned out to be quite a problem in the case of nitrogen. This problem was caused by the relatively strong curvature of the background on STE and, to a lesser extent, on LDE, especially on the short-wavelength side of the spectrum. The problem was solved by fitting the background, recorded on the pure metal element, to the nitride spectrum in a trial and error mode and then subtracting the proper fraction of this background from the spectrum of the unknown. Extensive use was hereby made of the built-in modules of the EDX system. Inspection of the resulting nitride spectrum usually showed a rather flat background on both sides of the N-K α peak which was then accessible to the normal procedure of linear interpolation. The background on STE was usually taken at ± 5.5 – 6.5 mm, depending on the curvature of the background; that on LDE at ± 10.5 mm. Another problem with background determination, especially on STE, was associated with the presence of remnants of higher order metal lines in the spectrum, e.g., 4th order Al-K α in AlN, 4th and 5th order Si-K α in Si₃N₄. Here too, trial and error procedures were used in which a fraction of the background of the pure element spectrum (Al or Si) was subtracted from the nitride spectrum. The success of the operation was judged from the disappearance of the interfering peak.

A major problem was the determination of APFs in compounds like TiN and Ti₂N: Due to the extreme overlap of the Ti- ℓ and N-K α peaks a straightforward measurement is out of the question here. In fact, a special procedure has been devised (Bastin and Heijligers 1988c) in the course of this work to measure the APF and to use this value in order to extract the Ti- ℓ peak from underneath the combined (Ti- ℓ + N-K α) peak. This will be discussed further on.

Finally, some remarks concerning the accuracies in the APF values seem appropriate. Due to the fact that the net peak count rates on STE can be extremely low, with peak-to-background ratios dropping well below 1, the experimental accuracy in APFs as claimed for our carbon measurements ($\pm 1\%$ relative), can most certainly not be matched here, in spite of the very large number of measurements performed. Our general feeling is that the accuracies for N-K α are probably in the order of $\pm 1.5\%$ for easy cases like BN, AlN, and Si₃N₄ and of 2–3% for really difficult cases like ZrN, Nb₂N, and Mo₂N.

Measurements of Integral k-Ratios Between 4 and 30 kV

Although the APF concept has been introduced (Bastin and Heijligers 1984, 1986a) in order to facilitate the conversion of fast (and usually incorrect) peak intensity ratios into correct integral intensity ratios with great savings of time and effort, the concept could only be used in a limited number of cases in the present work; viz for the nitrides of the lighter elements B, Al, and Si. The main reason was the sometimes strong curvature in the backgrounds in the heavier nitrides, which made the routine procedure, consisting of background measurements at equal distances on either side of the peak, impossible to use. Therefore, we were forced to perform the vast majority of the intensity measurements in a completely integral fashion, which was a very time-consuming procedure. The measurements themselves were carried out at 4, 6, 8, 10, 12, 15, 20, 25, and 30 kV. Despite the tedious nature of these integral measurements, the statistics are bound to be much poorer than those obtained in our usual approach in which a very large number of peak intensity ratio measurements can be carried out on a large number of different locations on the specimens in only a fraction of the time required for a single integral recording. The beam current used in all cases was 300 nA.

Because the net peak count rates and peak-to-background ratios on LDE were so much better than on STE and also the background on LDE was so much "cleaner," it was decided to average the final integral k-ratios on a 2:1 weight base in favour of LDE. All together, 144 k-ratios for N-K α relative to Cr₂N have been collected in this way to serve as the final database on which our matrix correction procedure has been applied.

The x-ray lines of the metal components have also been measured in all specimens and over the full range in voltage. All possible x-ray lines that could be excited (e.g., Ta-M α , Ta-L α) in the given range have been measured. The beam current was adjusted to give a maximum count rate of 3000 cps in order to avoid excessive dead time corrections. A total number of 149 k-ratios have finally been collected.

Results

Before discussing the actual numerical results of the present work, we would like to elaborate on two typical problems which we encountered.

The first (nasty) problem was the contamination with oxygen which occurred rapidly on sensitive nitrides and their constituent pure metals. The second problem was connected with the question how nitrogen can be measured in Ti-containing compounds. The Ti- ℓ line and the N-K α line overlap to such an extent that only one combined peak can be observed, thus making an independent analysis of nitrogen virtually impossible. In the course of the present work we developed and tested a new procedure for the separation of the Ti- ℓ and N-K α contributions, based on the use of the APF concept. Later on, it was found that the well-known multiple least-squares fitting techniques (McCarthy and Schamber 1981) could also be fruitfully used, especially in the analysis of low nitrogen contents.

Oxygen Contamination

Some results of this aspect of the present work have been published before (Bastin and Heijligers 1988a). It has been demonstrated that literally every nitride specimen can be oxidized under the electron beam, even without the use of an air jet. The relatively poor vacuum conditions in commercial microprobes, as compared with typical surface-analytical instruments, must be blamed for these oxygen contamination phenomena. The sensitivity to oxidation is, of course, strongly dependent on the specific nitride specimen and this is demonstrated in Table III where a compilation of the results is presented. Taking into consideration that the recording of an integral N-K α spectrum took something like 1.5 h, it is not surprising that the use of an air jet on specimens like HfN and ZrN will lead to disastrous results. Drops in the N-K α intensity after 1 h of more than 30% have been observed. Our observations on the N-K α count rate, which was monitored simultaneously with O-K α in the experiments of Table III, indicate that up to an increase of a factor of 2–3 in the O-K α count rate no noticeable losses in the N-K α count rate occur. It appears, therefore, that the long dwell times required for integral intensity measurements will not necessarily lead to losses in the N-K α intensity.

TABLE III Oxygen count rates, related to the initial count rates, on nitride specimens, as a function of time. (+ with air jet; - without air jet). 4 kV 300 nA

Compound	Time		
	1 min	5 min	50 min
AlN +	1.56	1.95	2.03
-	—	1.12	1.15
Si ₃ N ₄ +	1.39	1.37	1.39
-	1.23	1.98	2.10
TiN +	1.18	1.25	1.39
-	1.12	1.18	1.22
Ti ₂ N +	1.13	1.20	1.25
-	1.08	1.06	1.04
VN +	1.02	1.02	1.04
-	1.01	1.02	1.03
V ₂ N +	1.05	1.07	1.14
-	1.00	1.02	1.06
CrN +	1.12	1.39	2.02
-	0.99	0.99	1.06
Cr ₂ N +	1.02	1.17	1.76
-	1.08	1.12	1.25
Fe ₄ N +	1.18	1.27	1.46
-	1.04	1.07	1.18
ZrN +	2.42	3.80	6.84
-	1.78	2.54	3.39
Nb ₄ N ₃ +	1.19	1.20	1.25
-	1.02	1.04	1.10
Nb ₂ N +	1.00	1.03	1.04
-	1.00	0.99	1.05
Mo ₂ N +	0.94	1.02	1.16
-	1.04	1.02	1.08
HfN +	3.05	5.53	8.13
-	1.56	2.16	3.17
TaN +	1.80	2.87	4.81
-	1.65	1.68	1.93
Ta ₂ N +	1.18	1.63	3.21
-	1.06	1.05	1.07

Procedures for the Analysis of Nitrogen in the Presence of Titanium

One method we proposed earlier (Bastin and Heijligers 1988c) is based on the consideration that although the Ti- ℓ and N-K α peaks strongly overlap, they do not coincide completely. Hence, the combined peak must inevitably be broader than that of either of the contributors. This, in turn, should be noticeable in an increased value of the APF. If the correct value of the APF for Ti-N compounds were known, it could be used in a procedure in which increasing amounts of a Ti- ℓ spectrum are stripped from the combined peak in order to finally arrive at a residual N-K α peak with the specified APF. We have demonstrated that the APF can indeed be determined in an iterative fashion and that it can be used in a (time-consuming) procedure for quantitative EPMA of nitrogen in Ti-N compounds with a relative accuracy of better than 5%.

We also concluded that the well-known multiple least-squares deconvolution techniques, which are quite

common in EDX software, gave much less satisfactory answers. This was then attributed to the influence of the N-K absorption edge in the spectrum which gives rise to discontinuities in the background. Since then it has become clear to us that our negative experiences were also caused by two other effects. In the first place a very sophisticated version of such a program was originally used (TRACOR Northern), in which the first and second derivatives of the peaks were used in order to correct for possible peak shifts and peak shape alterations, respectively. In cases of strong overlap this approach does not necessarily lead to acceptable results. In the second place, our experiences with this software were confined only to N-rich compositions (25–50 at% N).

Quite some time later, however, when we were trying to analyze substantially lower nitrogen contents, we happened to test a much simpler version of a multiple least-squares program (TRACOR Northern, "Super ML," version XML-7k'/30) with surprisingly good results. In this particular program the first and second derivatives are not taken into account, and the filter width had the standard setting of 160 eV (16 channels) for the central lobe and 60 eV (6 channels) for the lower and upper lobes of the digital top hat filter. This program was found to perform remarkably well, even down to very low nitrogen levels where our APF procedure would fail due to a vanishing N-K α peak. This is demonstrated in Table IV for the case of a laser-nitrided Ti(Al,V) alloy. It is obvious that the Super ML program is able to detect very

low levels of nitrogen indeed, down to less than 0.2 wt%. The fact that zero values are sometimes found at long distances from the surface gives a lot of confidence in the technique. The surprisingly good quality of the fits for low nitrogen levels is not only expressed in very low χ^2 values in Table IV but can also be judged visually from Figure 1 where all steps of the fitting procedure are graphically represented for a composition of 1.37 wt% N in another (plasma-nitrided) alloy. It can be seen that after the subtraction of the Ti- α peak in the proper ratio a remaining N-K α peak is visible with its top at the correct position (compare with the Cr₂N spectrum). After the subtraction of this N-K α peak an almost ideally smooth background is obtained which shows only extremely weak signs of forming small dips on both sides of the N-K α peak. These dips become much more pronounced at much higher nitrogen levels, and must be attributed to small differences in peak widths between the N-K α peaks in standard and specimen. The same procedure when applied to spectra recorded with the STE crystal led to much poorer results. This must probably be attributed to the much better spectral resolution of this crystal which makes it much more sensitive to peak shifts and peak shape alterations.

Summarizing this paragraph we can say that quantitative analysis of nitrogen in Ti-containing compounds is definitely possible with a relative accuracy of better than 5% (for not too low levels). For nitrogen levels between 0 and 15 at% there is little choice between the two proce-

TABLE IV Results of the nitrogen analyses in a laser-nitrided Ti(V, Al) alloy using the Super ML multiple-least-squares digital fitting technique on spectra recorded with the LDE crystal at 10 kV and 300 nA

Distance from surface (μm)	χ^2	AKR N-K α	Wt% N	At% N
5	2.98	0.4440	4.17	12.95
5	2.88	0.3961	3.72	11.67
25	2.76	0.2577	2.42	7.81
25	2.40	0.3010	2.82	9.04
50	2.94	0.2713	2.55	8.20
50	2.68	0.3406	3.20	10.15
75	2.47	0.2733	2.56	8.26
75	2.46	0.3420	3.21	10.19
100	2.85	0.2946	2.77	8.86
100	2.42	0.2844	2.67	8.57
150	1.88	0.2302	2.16	7.01
150	2.12	0.2921	2.74	8.79
200	1.79	0.2181	2.00	6.66
200	2.10	0.2910	2.73	8.76
300	1.93	0.0414	0.39	1.32
300	1.85	0.0000	0.00	0.00
400	1.81	0.0160	0.15	0.51
475	1.86	0.0146	0.14	0.47
550	1.86	0.0194	0.18	0.62
760	2.02	0.0137	0.13	0.44

χ^2 is a statistical measure of success for the digital fit; a value close to 1 indicates an almost perfect fit. AKR is the area (integral) k-ratio relative to Cr₂N.

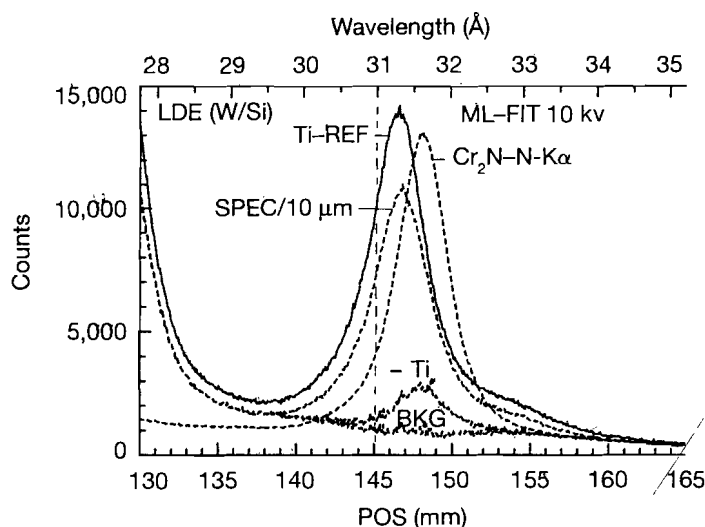


FIG. 1 Graphical representation of the Super ML fitting procedure applied to a spectrum recorded from a location 10 μm away from the surface in a plasma-nitrided Ti(Al,N) alloy. LDE crystal; 10 kV, 300 nA, 500 steps, counting time 3 s/step. Area k-ratio N-K α relative to Cr₂N 0.1458, corresponding to 1.37 wt% nitrogen (4.52 at%). $\chi^2 = 1.89$.

dures discussed here: The Super ML fitting procedure is the only option in this case and the simplest form of this program, in which no use is made of first and second derivatives, seems to give the best answers. For higher nitrogen levels there is a choice between the Super ML fitting technique and our APF Procedure. The former is the fastest technique although we have a slight preference for the APF procedure which gives slightly better and more consistent answers for the highest nitrogen contents. In all cases, however, the use of the LDE crystal has to be preferred.

Performance of LDE Crystal as Compared to Conventional Lead Stearate Crystal

The impressive improvement in performance of the LDE crystal in comparison to the STE crystal is best demonstrated for a notoriously difficult case: Nb₂N (Fig. 2). A number of conclusions can be drawn from this figure:

It is obvious that the LDE crystal brings an important improvement in the net count rates by approximately a factor of 2.8.

The peak-to-background ratio is significantly improved by a factor of 2–4.

The spectral resolution of the LDE crystal is slightly worse than that of the STE crystal, which may actually turn out to be an improvement in terms of the effects of peak shape alterations.

The LDE crystal is apparently able to produce a strong suppression of higher-order reflections. Although this

is apparent already in Figure 2 for Nb₂N, the strongest example we have seen so far is Fe₄N (Fig. 3), where the very strong second order Fe-L α line on STE is almost completely suppressed on LDE. The direct consequence of the suppression of interfering reflections is that much smoother and cleaner backgrounds are obtained which becomes all the more important in cases where count rates and peak-to-background ratios are extremely low already (ZrN, Nb₂N, Mo₂N, etc.).

It is important to note here that the strong suppression of higher order lines by the LDE crystal is not a universal feature of this crystal. According to our experiences with C, N, and O, it only takes place in the wavelength regions of the N-K α and O-K α peaks; in the region of the C-K α peak there is no sign of such an effect. In the latter case too, however, it can still be advantageous to use the LDE crystal despite its lower peak count rates for carbon than STE: In a number of cases, notably the lighter carbides like B₄C and SiC, the LDE crystal produces a smooth and horizontal background as compared to the kinked (B₄C) or strongly curved (SiC) background on STE.

The general conclusion of this comparison must be that the LDE crystal brings a most significant and genuine improvement in the quantitative analysis of nitrogen.

Area-Peak Factors for N-K α Relative to Cr₂N

Although we have stated before that the APF concept could only be used in a limited number of cases for fast routine measurements, in the present work it is nevertheless interesting to report the values we found; if only to make a comparison possible between the present results and those on boron, carbon, and (in the future) oxygen. We must emphasize again that in spite of the large number of measurements we cannot claim the same relative accuracy ($\pm 1\%$) which we claimed for our carbon measurements. Our feeling is that for the “easy” cases (BN, AlN, Si₃N₄) the accuracy is at the $\pm 1.5\%$ level; for the “difficult” cases (ZrN, Nb₂N, Mo₂N) it is probably ± 2 – 3% . Table V gives a survey of the observed values for both crystals. It will be clear from this table that the effects of peak shape alterations are very much less pronounced than for boron or even carbon. Nevertheless, shape alterations of +8% (BN on LDE) or –4% (Nb₂N on STE) are still something to be concerned about if one is interested in quantitative analysis. Furthermore, it is interesting to point out that in spite of the small effects still something of a saw-tooth like variation of APF with atomic number of the metal partner is visible, similar to the observations in borides and carbides. Again, very stable compounds like TiN and ZrN hold absolute minimum values while highly unstable nitrides like Mo₂N have among the highest values.

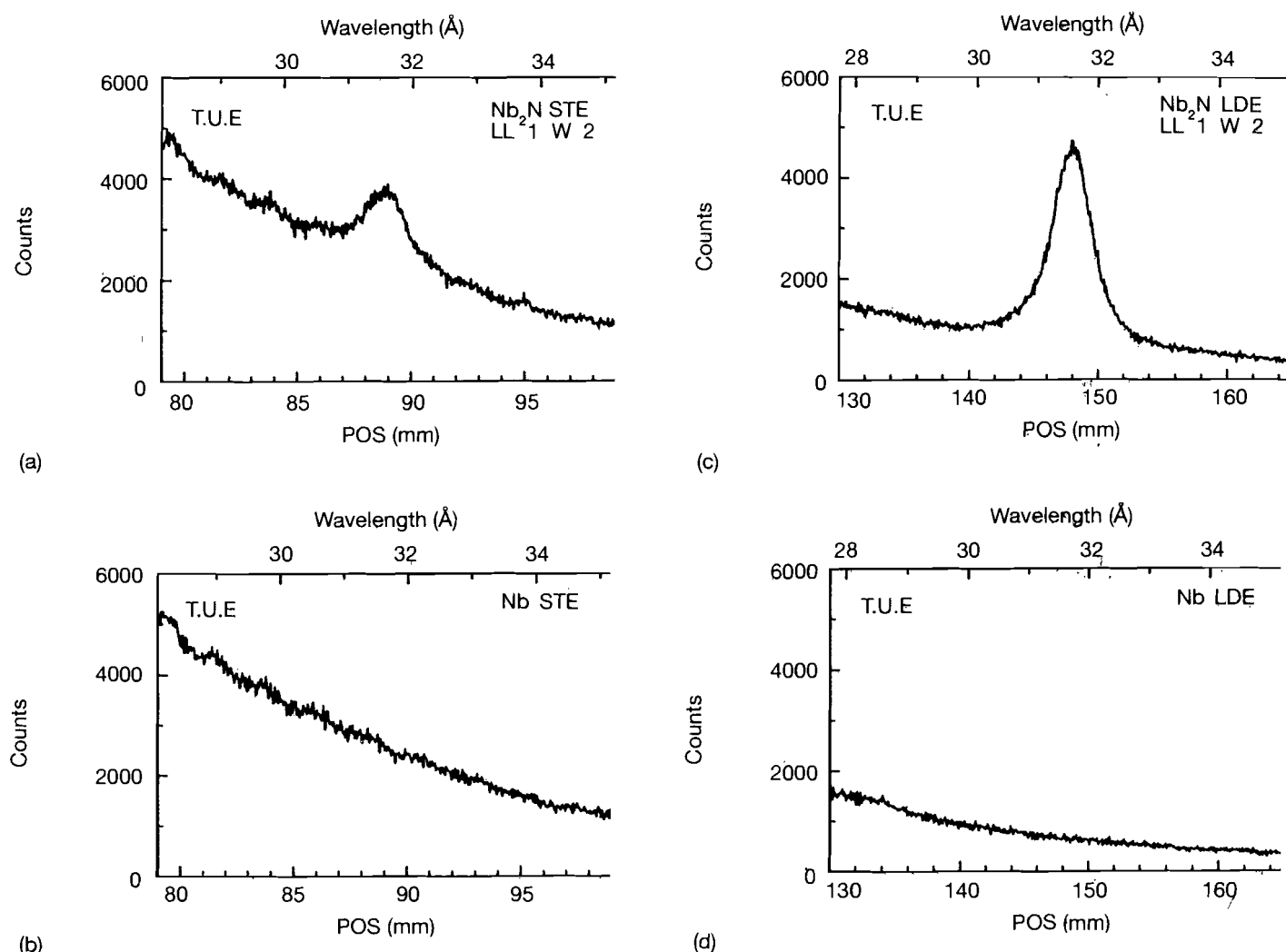


FIG. 2 Nitrogen spectra recorded from Nb_2N (top) and elemental Nb (bottom). Left-hand side conventional lead-stearate crystal; right-hand side new multilayer crystal (W/Si). Experimental conditions: 10 kV, 300 nA, counting time per channel 10 s, pulse height 2.0 V, lower level 1.0 V, window 2.0 V.

Conductivity Problems in Some Nitride Specimens

Figure 4 reflects another problem, hardly discussed until now: the lack of electrical conductivity in some nitride specimens. Hexagonal BN (open squares) was the worst example we encountered so far in this respect, although we had some problems too with AlN and Si_3N_4 . The influence of a lack of electrical conductivity on the quantitative results of EPMA has been discussed in detail in one of our previous publications (Bastin and Heijligers 1988b). It has been shown that the application of a conductive (carbon) coating will not necessarily lead to meaningful results, not even when a hole is burned in the conductive coating with the help of an air jet, as we have done for hexagonal BN in Figure 4. It is obvious that the conductive cubic form of BN shows a different variation of emitted intensity with voltage than the hexagonal one, suggesting at first sight a different MAC of $\text{N-K}\alpha$ in both forms of BN. The problems with the nonconducting hexagonal form of BN not only manifested themselves in

a deviating behaviour of the emitted intensity with varying voltage, but also in an abnormal variation of k-ratio with accelerating voltage. It proved virtually impossible to obtain agreement between the observed k-ratios and the predictions made by our correction program "PROZA" (Bastin and Heijligers 1990), not only for $\text{N-K}\alpha$ but also for $\text{B-K}\alpha$. Attempts to perform the measurements on carbon-coated samples (standard as well as specimen) were only partly successful: only the voltage range around 10 kV yielded anywhere near acceptable results. Outside this range, however, large deviations were usually observed. All efforts to perform the measurements through a hole burned in the carbon coating using an air jet failed to produce acceptable results.

As soon as the measurements could be carried out on cubic BN with much better electrical conductivity, good agreement was again found between predictions and observations without the use of any coating.

The measurements on Si_3N_4 could be performed quite successfully through holes burned in a carbon coating.

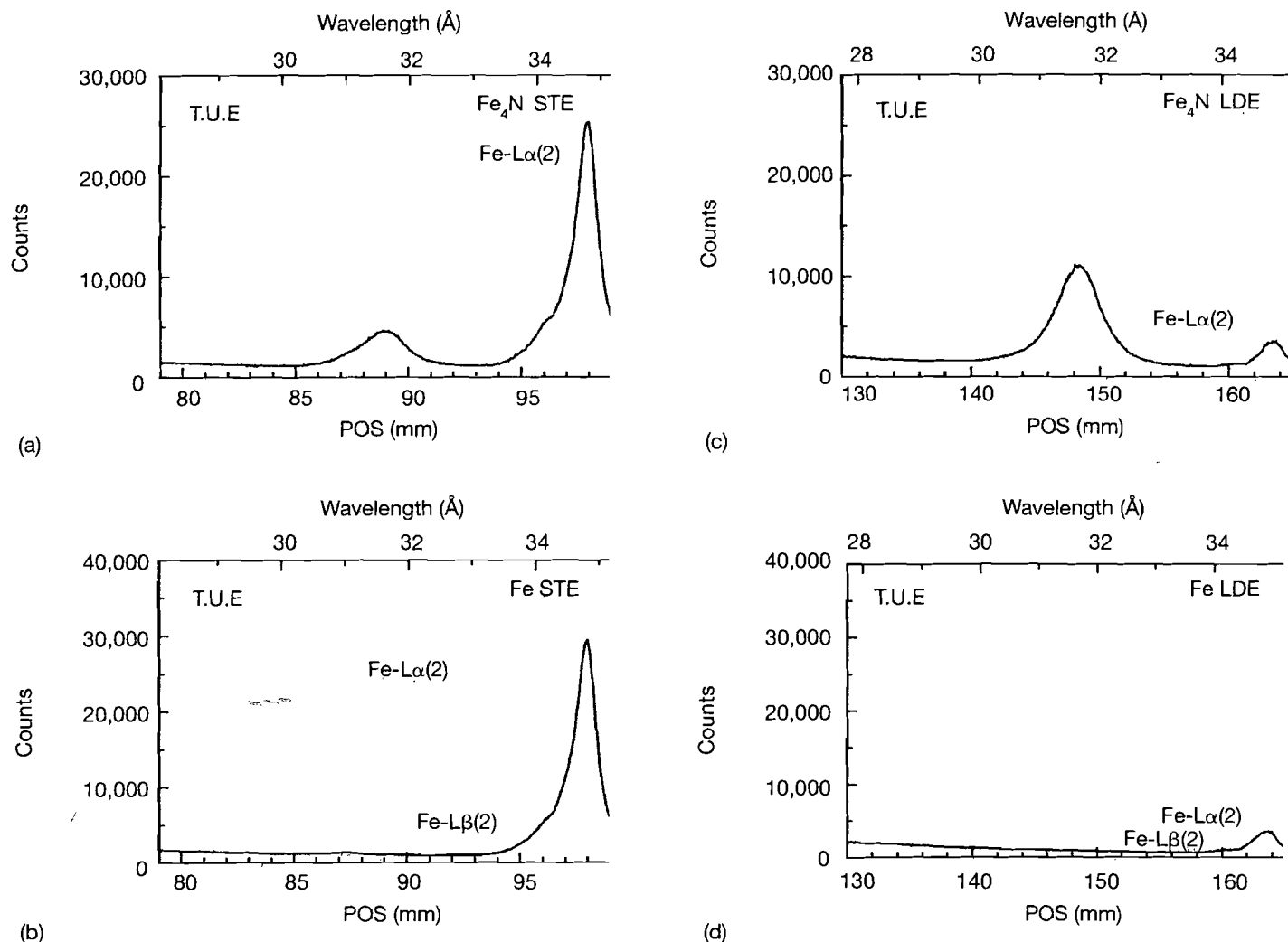


FIG. 3 Nitrogen spectra recorded from Fe₄N (top) and elemental Fe (bottom). Left-hand side conventional lead-silicate crystal; right-hand side new multilayer crystal (W/Si). Experimental conditions: 10 kV, 300 nA, counting time per channel 10 s, pulse height 2.0 V, lower level 1.0 V, window 2.0 V.

Apparently the presence of a well-conducting Si-substrate underneath the 2.5 μm Si₃N₄ layer provides sufficient "relief" to the incoming electrons as to prevent serious charging effects inside the specimen. Possible slight surface charging effects are obviously alleviated by the presence of the remaining carbon coating surrounding the hole.

The measurements on AlN could be carried out without any coating at all. However, small voltage drops did occur at the specimen surface due to charging. This was established by recording the short-wavelength cut-off at the CRT of the EDX system. The corrected voltages have been used in the final database (see Appendix).

Data Reduction

Once the intensities have been correctly measured and a reliable database has been obtained, the final step is, of

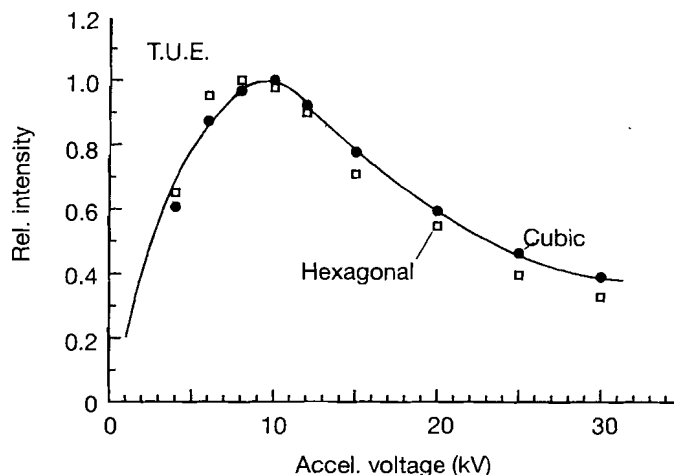


FIG. 4 Relative N-K α intensity emitted from hexagonal (open squares) and cubic (full circles) BN as a function of accelerating voltage.

TABLE V Area-peak factors for N-K α relative to Cr₂N (Batch 1) for the nitrides of the present investigation. The numbers in parentheses refer to the number of measurements involved

Compound	Area-peak factor			
	STE		LDE	
BN (Hex)	1.0522	(77)	1.1010	(5)
	—	—	1.0820	(7)
AlN	0.9829	(36)	0.9825	(7)
Si ₃ N ₄	1.0707	(78)	1.0838	(6)
Ti ₂ N	0.9710	^a	0.9800	^a
TiN	0.9710	^a	0.9800	^a
V ₂ N	0.9948	(80)	0.9960	(70)
VN	1.0048	(81)	1.0048	(71)
Cr ₂ N	1.0000	Def.	1.0000	Def.
CrN	1.0180	(75)	1.0180	(62)
Fe ₄ N	1.0318	(33)	0.9941	(12)
ZrN	0.9644	(88)	0.9778	(68)
Nb ₂ N	0.9599	(101)	0.9969	(84)
Nb ₄ N ₃	1.0135	(112)	1.0207	(94)
Mo ₂ N	1.0572	(139)	1.0334	(96)
HfN	0.9732	(90)	0.9841	(77)
Ta ₂ N	0.9695	(90)	0.9806	(77)
TaN	0.9751	(90)	0.9863	(76)

^a These results have been obtained during the development of our APF procedure for the analysis of nitrogen in Ti-N compounds

course, the conversion of k-ratios into concentrations. We have already pointed out that this can only be done with a good matrix correction program in conjunction with a consistent set of MACs. Our experiences with databases for B-K α and C-K α have shown that the available sets of MACs in literature (Henke and Ebisu 1974, Henke *et al.* 1982) will not lead to acceptable results for any of the existing matrix correction programs. In our opinion this points to inconsistencies in the available sets, and this is most frequently the case for the elements Zr, Nb, and Mo. In these elements, the wavelengths of the ultraviolet element radiations are very close to the M-absorption edge and this gives rise to a strongly curved variation of MAC with wavelength. Hence, it is very dangerous and difficult to carry out calculations and extrapolations in this region. This presumably also explains why there are sometimes such large differences in individual values between the older and newer sets published by Henke and co-workers. We have frequently found it necessary to adjust specific MACs in order to get more consistent results, and it was not uncommon to find that the new optimum values are somewhere between the older and newer values published by Henke. This also has been the case in the present work. During our exercises with our database in which our own proven correction program "PROZA" was used and various sets of MACs were tested, we arrived at a new and much more consistent set (Table VI), the use of which led to significantly improved results, not only for our "PROZA" program, but for virtually any widespread correction program. It is clear that for the elements Zr, Nb, and Mo the new values we propose are closer to the older values of Henke and

TABLE VI Mass absorption coefficients for N-K α x-rays according to various sources

Absorber	Henke (1974)	Henke (1982)	Present work
B	15,810	15,800	15,800
N	1,637	1,810	1,810
Al	13,830	13,800	13,100
Si	17,690	16,500	17,170
Ti	4,364	4,360	4,360
V	4,790	4,790	4,790
Cr	5,630	5,630	5,630
Fe	7,121	7,190	7,190
Zr	25,030	20,400	24,000
Nb	27,190	21,400	25,000
Mo	23,220	20,200	25,000
Hf	12,910	12,900	14,050
Ta	13,420	13,400	15,000

Ebisu (1974). In addition, we found it necessary to propose much higher values for Hf and Ta.

The use of the MACs in Table VI led to surprisingly good results for the individual sets of measurements (see Appendix) as Table VII shows. For the lighter nitrides (BN up to TiN) the measurements were exclusively performed with the STE crystal. From V₂N on both STE and LDE crystals were used simultaneously. In the latter cases the final k-ratios for N-K α were obtained by weighting the results in a 2:1 ratio in favour of LDE. Figure 5 shows the histogram obtained with "PROZA" on the database of 144 (unsmoothed) k-ratios for N-K α using the MACs of Table VI. Some graphical repre-

TABLE VII Numerical results obtained in the individual sets of intensity measurements of the x-ray lines of the metals and nitrogen in the nitride specimens of the present investigation between 4 and 30 kV. k' is the calculated k-ratio and k the measured one. RMS is the relative root mean square deviation in %

Compound	Line	Metal analysis		Nitrogen analysis	
		Av. k'/k	RMS %	Av. k'/k	RMS %
BN (cub)	B-K α	0.9722	1.3966	0.9989	5.9150
AlN	Al-K α	0.9867	0.6667	0.9867	3.4641
Si ₃ N ₄	Si-K α	0.9900	0.0000	1.0033	6.9121
Ti ₂ N	Ti-K α	0.9725	0.4330	0.9856	3.2356
TiN	Ti-K α	0.9725	0.4330	0.9922	2.8588
V ₂ N	V-K α	0.9800	0.000	1.0089	2.0245
VN	V-K α	0.9800	0.0000	1.0056	1.7069
Cr ₂ N	Cr-K α	0.9914	0.3499	—	—
CrN	Cr-K α	0.9871	0.6999	0.9911	1.0999
Fe ₄ N	Fe-K α	1.0100	0.0000	1.0322	1.4741
ZrN	Zr-L α	0.9689	0.3143	1.0244	2.6713
Nb ₂ N	Nb-L α	0.9911	0.5666	1.0367	4.4222
Nb ₄ N ₃	Nb-L α	0.9878	0.4157	0.9922	2.8197
Mo ₂ N	Mo-L α	1.0011	0.8749	1.0267	5.0990
HfN	M/L- α	1.0022	0.6285	1.0022	1.9309
Ta ₂ N	Ta-M α	0.9878	0.4157	0.9956	4.4500
Ta ₂ N	Ta-L α	1.0000	0.0000	—	—
TaN	Ta-M α	0.9944	0.6849	1.0000	2.7487
TaN	Ta-L α	1.0100	0.8944	—	—
Overall results:					
Metals analyses (149 entries): $k'/k=0.9880$		RMS = 1.3259%			
Nitrogen analyses (144 entries): $k'/k=1.0051$		RMS = 3.9965%			

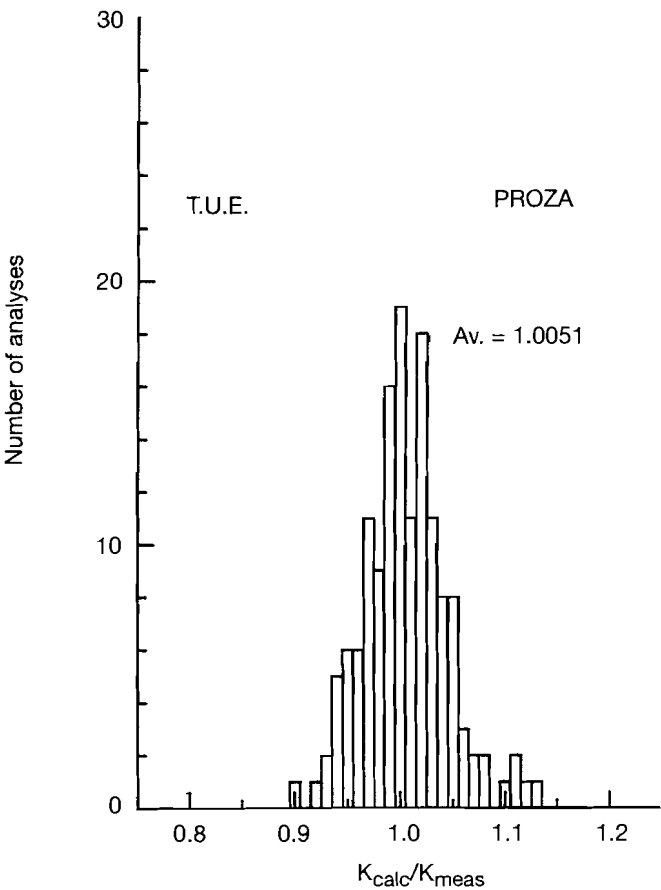


FIG. 5 Histogram obtained with our “PROZA” program on a database of 144 nitrogen analyses between 4 and 30 kV. Mass absorption coefficients of Table VI were used. RMS = 3.99%.

sentations of our measurements are given in Figure 6 (Fe₄N and ZrN) and Figure 7 (Mo₂N and HfN) where they are compared to the predictions of our program. It is obvious that the program performs remarkably well up to accelerating voltages as high as 30 kV. The discrepancies between the predicted and the experimentally obtained k-ratios rarely exceed 5% relative, even in the most difficult cases like ZrN, Nb₂N and Mo₂N. This is all the more remarkable because the integral measurements for each compound as a function of voltage were obtained over a 2-week period in most cases, and as a result, one would expect a somewhat larger scatter than from a continuous (1-day) measurement.

Conclusions

A number of general conclusions can be drawn from the present work: First, accurate intensity measurements are possible for N-K α radiation over a wide range in accelerating voltages, despite the fact that this particular element is by far the most difficult to deal with in the sequence of the ultralight elements B, C, N, and O.

The use of a modern synthetic multilayer crystal (W/Si, 2d = 5.98 nm) gives a major improvement in this respect, since it can provide 2.8 times higher net peak intensities. At the same time, however, it can produce a strong suppression of higher-order reflections which is

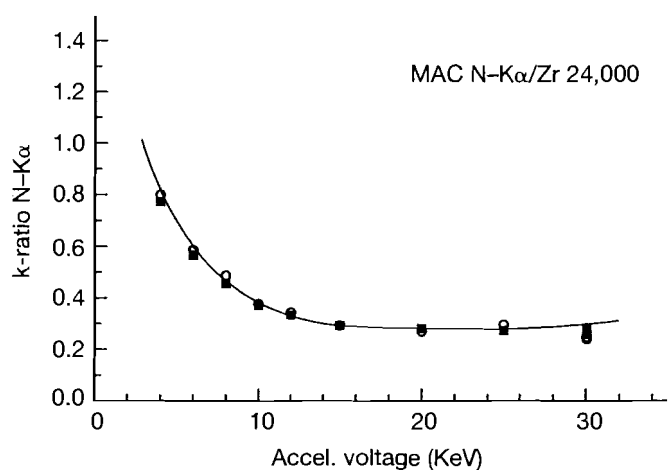
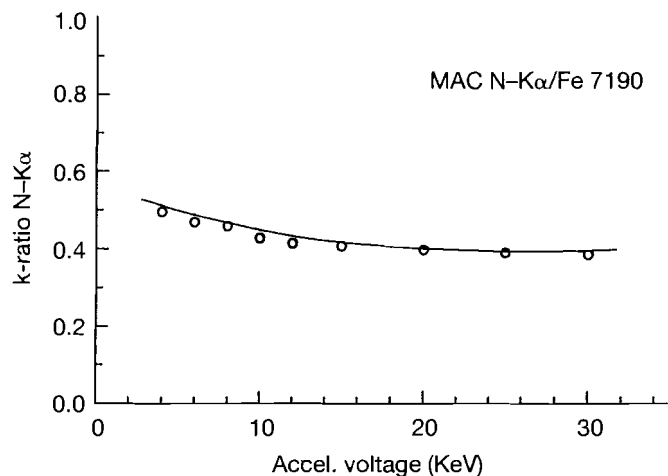


FIG. 6 Comparison between the experimental integral k-ratios for N-K α relative to Cr₂N and the predictions of our "PROZA" program (solid curve). Top: uncoated Fe₄N; bottom: uncoated ZrN. Circles indicate the results of the stearate; solid squares those of the LDE crystal.

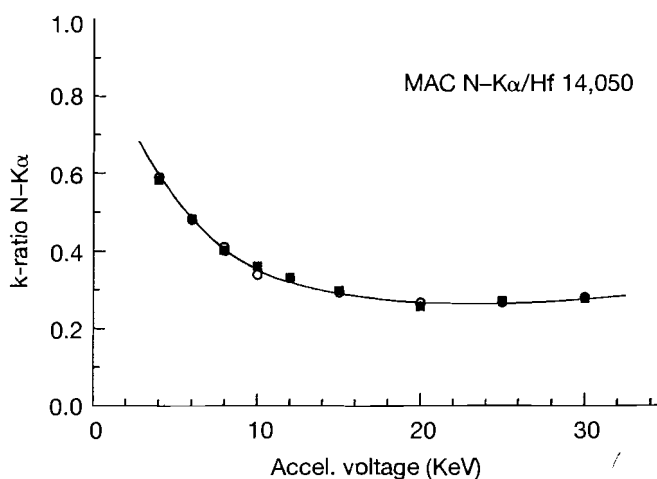
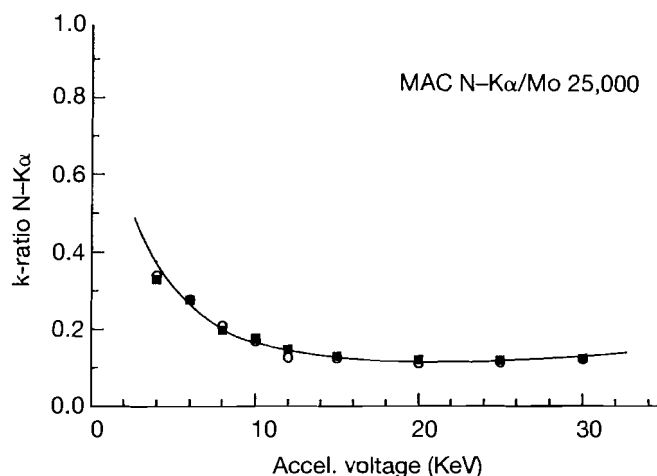


FIG. 7 Comparison between the experimental integral k-ratios for N-K α relative to Cr₂N and the predictions of our "PROZA" program (solid curve). Top: uncoated Mo₂N; bottom: uncoated HfN. Circles indicate the results of the stearate; solid squares those of the LDE crystal.

extremely beneficial for the accurate determination of the backgrounds.

Second, reasonably accurate (better than 5% relative) analysis of nitrogen appears to be possible even in Ti-containing compounds, in spite of the severe overlap of the Ti- β and the N-K α peaks. In this respect, too, the application of the W/Si multilayer crystal leads to major improvements in the results.

Peak shape alterations in the N-K α peak, relative to a Cr₂N standard, are much smaller than those observed for B-K α and C-K α radiations: The APF values were found to differ less than 5% from unity. Nevertheless, for accurate quantitative analysis these effects have to be taken into account.

Our latest Gaussian $\varphi(\rho z)$ correction program "PROZA" produces excellent results on the newly collected database of 144 N-K α measurements between 4 and 30 kV. Since the results are equally satisfactory on previously collected ultralight element data as well as on medium-to-high Z element data, the conclusion seems

justified that this particular program is a genuine step forward toward the ultimate goal of a "universal" correction program.

The overall conclusion of the present work can be that accurate quantitative analysis of nitrogen is definitely possible, provided that the measurements are performed carefully, a good correction program is used and, not in the last place, a consistent set of mass absorption coefficients is used.

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Appendix

Numerical details of the final database containing the unsmoothed Integral k-ratios for N-K α relative to Cr₂N (Batch 1) and the smoothed peak k-ratios for the metal x-ray lines relative to elemental standards.

Legend:

1st column	Number of elements - 1									
2nd column	Atomic number of chief metal component									
3rd column	Atomic number of second metal component									
4th column	Weight fraction of chief metal component									
5th column	Weight fraction of nitrogen									
6th column	Weight fraction of second metal component, note that the weight fraction of oxygen is obtained as 1—the sum of columns 4-6									
7th column	k-ratio of chief metal component x-ray line									
8th column	k-ratio of N-K α relative to Cr ₂ N									
9th column	Accelerating voltage (kV)									
10th column	Type of x-ray line of chief metal component (K = 0, L = 1, M = 2)									
11th column	Type of x-ray line of second metal component (K = 0, L = 1, M = 2)									

1	5	0	0.4355	0.5645	0.0000	0.2856	3.0746	8.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.2539	2.9503	10.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.2316	2.7111	12.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.2049	2.4133	15.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.1823	2.1520	20.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.1800	1.9887	25.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.1834	1.9663	30.00	0	0
1	13	0	0.6582	0.3418	0.0000	0.6220	2.4707	3.38	0	0
1	13	0	0.6582	0.3418	0.0000	0.6218	2.1717	5.01	0	0
1	13	0	0.6582	0.3418	0.0000	0.6195	2.0145	6.92	0	0
1	13	0	0.6582	0.3418	0.0000	0.6160	1.7870	8.56	0	0
1	13	0	0.6582	0.3418	0.0000	0.6100	1.7170	10.64	0	0
1	13	0	0.6582	0.3418	0.0000	0.6010	1.5166	13.92	0	0
1	13	0	0.6582	0.3418	0.0000	0.5800	1.3502	18.28	0	0

1	5	0	0.4355	0.5645	0.0000	0.1823	2.1520	20.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.1800	1.9887	25.00	0	0
1	5	0	0.4355	0.5645	0.0000	0.1834	1.9663	30.00	0	0
1	13	0	0.6582	0.3418	0.0000	0.6220	2.4707	3.38	0	0
1	13	0	0.6582	0.3418	0.0000	0.6218	2.1717	5.01	0	0
1	13	0	0.6582	0.3418	0.0000	0.6195	2.0145	6.92	0	0
2	14	0	0.6006	0.3924	0.0000	0.5640	2.3694	4.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5655	2.0676	6.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5660	1.9246	8.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5640	1.7510	10.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5625	1.6467	12.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5570	1.4099	15.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.5450	1.1097	20.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.0000	1.1738	25.00	0	0
2	14	0	0.6006	0.3924	0.0000	0.0000	1.0954	30.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.0000	1.0960	4.00	1	0
1	22	0	0.8816	0.1184	0.0000	0.8630	1.2060	6.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8662	1.2320	8.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8695	1.2520	10.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8719	1.3450	12.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8750	1.3560	15.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8792	1.3640	20.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8816	1.5220	25.00	0	0
1	22	0	0.8816	0.1184	0.0000	0.8820	1.5240	30.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.0000	2.1360	4.00	1	0
1	22	0	0.7750	0.2250	0.0000	0.7300	2.2210	6.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7345	2.3320	8.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7390	2.3575	10.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7425	2.5880	12.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7480	2.5160	15.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7538	2.6820	20.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7582	2.7540	25.00	0	0
1	22	0	0.7750	0.2250	0.0000	0.7605	3.0230	30.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.0000	1.1588	4.00	1	0
2	23	0	0.8723	0.1199	0.0000	0.0000	1.1965	6.00	1	0
2	23	0	0.8723	0.1199	0.0000	0.8460	1.1960	8.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8500	1.2329	10.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8530	1.2620	12.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8560	1.2774	15.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8618	1.3130	20.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8640	1.2619	25.00	0	0
2	23	0	0.8723	0.1199	0.0000	0.8650	1.2861	30.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.0000	1.5671	4.00	1	0

2	23	0	0.8365	0.1604	0.0000	0.0000	1.5830	6.00	1	0
2	23	0	0.8365	0.1604	0.0000	0.8000	1.6286	8.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8038	1.6468	10.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8068	1.6662	12.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8110	1.7217	15.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8162	1.7396	20.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8200	1.7528	25.00	0	0
2	23	0	0.8365	0.1604	0.0000	0.8215	1.7496	30.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8518	0.0000	8.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8595	0.0000	10.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8635	0.0000	12.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8680	0.0000	15.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8740	0.0000	20.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8783	0.0000	25.00	0	0
2	24	0	0.8882	0.1070	0.0000	0.8805	0.0000	30.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.0000	1.9261	4.00	1	0
1	24	0	0.7878	0.2122	0.0000	0.0000	1.9679	6.00	1	0
1	24	0	0.7878	0.2122	0.0000	0.7290	2.0171	8.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7365	2.0027	10.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7433	2.0406	12.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7505	2.0765	15.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7595	2.0702	20.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7650	2.1528	25.00	0	0
1	24	0	0.7878	0.2122	0.0000	0.7685	2.0806	30.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.0000	0.4941	4.00	1	0
1	26	0	0.9440	0.0560	0.0000	0.0000	0.4688	6.00	1	0
1	26	0	0.9440	0.0560	0.0000	0.9118	0.4587	8.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9140	0.4226	10.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9173	0.4154	12.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9202	0.4075	15.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9240	0.3975	20.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9260	0.3898	25.00	0	0
1	26	0	0.9440	0.0560	0.0000	0.9270	0.3853	30.00	0	0
2	40	0	0.8663	0.1270	0.0000	0.8235	0.7799	4.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8308	0.5771	6.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8365	0.4642	8.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8420	0.3713	10.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8465	0.3378	12.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8518	0.2934	15.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8583	0.2765	20.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8637	0.2816	25.00	1	0
2	40	0	0.8663	0.1270	0.0000	0.8660	0.2768	30.00	1	0

2	41	0	0.9299	0.0655	0.0000	0.9042	0.4104	4.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9068	0.2785	6.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9097	0.2298	8.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9120	0.1914	10.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9130	0.1612	12.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9140	0.1334	15.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9158	0.1275	20.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9162	0.1327	25.00	1	0
2	41	0	0.9299	0.0655	0.0000	0.9165	0.1300	30.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8520	0.6129	4.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8578	0.4381	6.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8618	0.3444	8.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8650	0.2913	10.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8682	0.2457	12.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8722	0.2234	15.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8763	0.2111	20.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8793	0.2210	25.00	1	0
2	41	0	0.8949	0.0979	0.0000	0.8800	0.2129	30.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.8964	0.3315	4.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9023	0.2754	6.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9078	0.1899	8.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9122	0.1737	10.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9163	0.1411	12.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9220	0.1278	15.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9298	0.1166	20.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9360	0.1165	25.00	1	0
1	42	0	0.9420	0.0580	0.0000	0.9399	0.1227	30.00	1	0
3	72	40	0.9136	0.0606	0.0229	0.8537	0.5835	4.00	2	1
3	72	40	0.9136	0.0606	0.0229	0.8655	0.4813	6.00	2	1
3	72	40	0.9136	0.0606	0.0229	0.8728	0.4028	8.00	2	1
3	72	40	0.9136	0.0606	0.0229	0.8783	0.3528	10.00	2	1
3	72	40	0.9136	0.0606	0.0229	0.8584	0.3300	12.00	1	1
3	72	40	0.9136	0.0606	0.0229	0.8694	0.2951	15.00	1	1
3	72	40	0.9136	0.0606	0.0229	0.8792	0.2586	20.00	1	1
3	72	40	0.9136	0.0606	0.0229	0.8821	0.2694	25.00	1	1
3	72	40	0.9136	0.0606	0.0229	0.8883	0.2763	30.00	1	1
2	73	0	0.9629	0.0347	0.0000	0.9505	0.3379	4.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9518	0.2660	6.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9522	0.2207	8.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9534	0.1930	10.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9540	0.1767	12.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9558	0.1662	15.00	2	0

2	73	0	0.9629	0.0347	0.0000	0.9580	0.1501	20.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9600	0.1562	25.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9620	0.1600	30.00	2	0
2	73	0	0.9629	0.0347	0.0000	0.9343	0.0000	12.00	1	0
2	73	0	0.9629	0.0347	0.0000	0.9375	0.0000	15.00	1	0
2	73	0	0.9629	0.0347	0.0000	0.9400	0.0000	20.00	1	0
2	73	0	0.9629	0.0347	0.0000	0.9422	0.0000	25.00	1	0
2	73	0	0.9629	0.0347	0.0000	0.9440	0.0000	30.00	1	0
2	73	0	0.9327	0.0651	0.0000	0.8843	0.6149	4.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.8900	0.5130	6.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.8942	0.4307	8.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.8983	0.3778	10.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.9022	0.3398	12.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.9071	0.2823	15.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.9142	0.2725	20.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.9190	0.2668	25.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.9220	0.2917	30.00	2	0
2	73	0	0.9327	0.0651	0.0000	0.8640	0.0000	12.00	1	0
2	73	0	0.9327	0.0651	0.0000	0.8740	0.0000	15.00	1	0
2	73	0	0.9327	0.0651	0.0000	0.8860	0.0000	20.00	1	0
2	73	0	0.9327	0.0651	0.0000	0.8940	0.0000	25.00	1	0
2	73	0	0.9327	0.0651	0.0000	0.8980	0.0000	30.00	1	0