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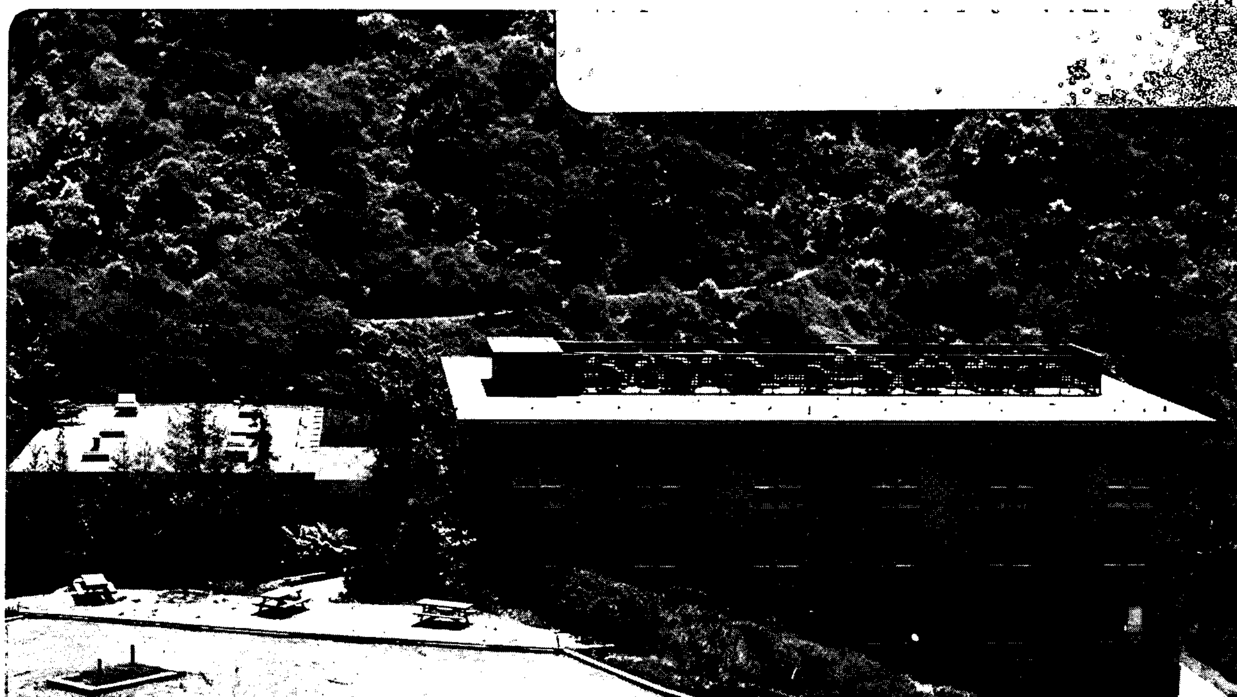

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DETERMINATION OF UTW K_{XSi} FACTORS FOR LOW ATOMIC NUMBER MICROANALYSIS: A SYSTEMATIC APPROACH

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DETERMINATION OF UTW K_{XSi} FACTORS FOR LOW ATOMIC NUMBER MICROANALYSIS: A SYSTEMATIC APPROACH

Kannan M. Krishnan and C. J. Echer

A systematic measurement of experimental K_{XSi} factors, with particular emphasis on low Z microanalysis ($6 \leq Z \leq 32$), at 200kV for a KEVEX UTW Si(Li) detector fitted to a JEOL 200CX analytical microscope, using a variety of high purity standards has been carried out. Under normal operating conditions of a LaB_6 filament, it is shown that absorption in the specimen is very critical, particularly for heavy element matrices, and sample thicknesses need to be measured for accurate microanalysis of low Z elements (C,N,O). Using these measured K_{XSi} factors, quantitative UTW-EDX microanalysis has been routinely extended to carbon.

Introduction

Quantitative X-ray microanalysis in an analytical electron microscope equipped with a Si(Li) detector can be performed by relating the measured X-ray intensities to the elemental weight fractions using the ratio method proposed by Cliff and Lorimer [1]:

$$\frac{C_A}{C_B} = \frac{k_B}{k_A} \frac{I_A}{I_B} = K_{AB} \frac{I_A}{I_B} = \frac{K_{ASi}}{K_{BSi}} \frac{I_A}{I_B} . \qquad (1)$$

The authors are at the National Center for Electron Microscopy, Lawrence Berkeley Laboratory, Berkeley, CA 94720. For specimen preparation and photography, the authors are indebted to Wendy Smith and John Turner, respectively, without whose help this project would not have been completed. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

The Cliff-Lorimer K-factors, K_{AB} are normally determined with respect to silicon (K_{XSi}). The term k_A for any particular element A, is a product of the relevant X-ray generation parameters and an instrument dependent efficiency parameter. It is given by

$$k_A = \frac{Q_A \omega_A a_A}{W_A} \eta_A \qquad (2)$$

where Q_A is the ionization cross-section, ω_A is the fluorescence yield, a_A is the radiative branching ratio, W_A is the atomic weight and η_A is the efficiency of detection. It is possible to calculate these K-factors if the cross-section used for inner shell ionizations are reliable and the detector and window parameters that determine its efficiency are well known [2,3]. On the other hand, these K factors can also be determined experimentally for a particular microscope and for a fixed acceleration voltage, provided that suitable thin film standards can be obtained [4,5]. The merits of each of these approaches have been a subject of considerable debate [2].

Two representative spectra of a NiO film obtained with a newly installed UTW (100nm parylene + 100nm aluminium) and after about ~ 600 hours of operation are shown in Figure 1. The deterioration in the performance of the window can be clearly attributed to water vapour contamination--the preferential absorption of the Ni-L lines compared to the O-K lines is largely due to the low self-absorption of the O-K X-rays in water vapour. Figure 2 shows two spectra obtained at different thicknesses from the same sample of AlN. For normal operating conditions using a LaB_6 filament, we observe that the samples have to be ~ 100nm thick to obtain a count rate of ~500-1000 cps when a 60nm diam. probe is used. Notice that even for 200nm

thick samples, substantial absorption of N-K X-rays in the specimen is observed. For x-rays of lower energy (C-K), absorption in the specimen is far more severe. Hence, the thin film criterion is not valid and appropriate corrections for absorption in the specimen have to be included in the microanalysis. It has been conservatively estimated [6] that absorption of O-K X-rays becomes critical for specimens that are >10nm thick. These observations coupled with the paucity of reliable cross-section data have convinced us to take the experimental approach. Our measurements of K_{XSi} factors at 200kV for low atomic number elements ($Z > 6$), including corrections for absorption in the specimen using standard KEVEX 8000 software, are presented here.

Experimental

All measurements were made on a JEOL 200CX TEM/STEM analytical microscope operating at 200kV and fitted with a horizontal KEVEX UTW detector with a nominal resolution (FWHM) of 109eV for F-Kα X-rays. The window and detector parameters of relevance (supplied by the manufacturer) were: parylene film (100nm); aluminium coating (100nm); gold contact layer (200nm); silicon dead layer (0.1μm) and silicon active layer (2mm). High purity polycrystalline and single crystal stoichiometric ceramic standards were purchased from commercial manufacturers [7,8]. The carbides were obtained from Oak Ridge National Laboratory [9]. The microtomed mineral standards were obtained from NASA Ames Laboratory [10]. All specimens were first mechanically thinned and then ion-milled to perforation. The samples were either self supporting or mounted on Beryllium grids. A comprehensive list of standards used for measurements of K_{XSi} along with the measured compositions are shown in Table 1. Characteristic X-ray spectra were acquired using a probe of ~60 nm diameter, an emission current of ~20-30μamps and an average counting time of

~600-1000 seconds to obtain good statistics. To avoid any channeling effects [11], the specimen was tilted to an orientation in which no lower order Bragg diffraction vectors were excited (Fig. 2). The foil thickness at each data acquisition point was measured generally by the convergent beam electron diffraction fringe method [12] and in some cases (amorphous films), by the contamination spot separation method [13]. A low background Be specimen holder (GATAN Model 636), cooled to LN_2 temperatures for crystalline specimens was used for all the specimen measurements. A typical set of data from a sample of AlN is shown in Fig 2.

Discussion

Experimentally determined K_{XSi} factors for all the elements studied ($6 \leq Z \leq 33$) are summarized in Table 1. The data pertains to the K shell and the total shell is included in the measurements. Theoretical values of K_{XSi} for the UTW detector were also calculated using the Zaluzec parametrization [14] of the Bethe cross-section [15]. Absorption corrections for all experimental data have been calculated using an iterative program that was part of the KEVEX 8000 software package (TEMSTAR). These results are plotted in Fig. 3. In the same figure our results are compared with the UTW results of Thomas [16], Cliff et al. [17] and Wirmak et al. [18]. There was considerable deviation of the experimental measurements from the calculated values using the detector parameters supplied by KEVEX. However, the detector parameters can be varied in an iterative manner and a good match (Fig. 3) between experimentally measured and calculated K-factors can be obtained, particularly for elements of atomic number $12 \leq Z \leq 33$. Our best results were obtained for the following UTW detector parameters: parylene window ~0.1μm, aluminum coating ~0.15μm, gold contact layer ~20.0nm and silicon dead layer ~0.125μm. It can be seen (Fig. 3) that the calculations,

though accurate for $12\leq Z\leq 33$, cannot predict K_{XSi} for $Z\leq 10$, making experimental measurements absolutely essential for accurate low Z (C,N,O) microanalysis. Note that absorption in the specimen has to be included for UTW detectors attached to microscopes operating with LaB_6 filaments. However, these detector parameters measured can be used to calculate K_{XSi} factors for $12\leq Z\leq 33$ at any other acceleration voltage.

Analysis of NBS standards [19]

A sputter deposited glass film standards (NBS K-411) and a microtomed glass film (NBS K-412) were used to check the accuracy of the experimentally measured K_{XSi} factors. The results of our microanalysis are compared with the original NBS analysis in Table 2. Even though the NBS analysis did not include oxygen, their concentrations of oxygen determined by stoichiometry seem to be in good agreement with our analysis using the K_{XSi} factors in Table 1.

Conclusion

Experimental K_{XSi} factors for low atomic number elements ($Z > 6$) for a JEOL 200CX AEM operating at 200kV and fitted with a KEVEX UTW detector have been determined. In the course of these measurements, relevant UTW detector parameters were estimated to calculate K_{XSi}. These calculated values agree very well with the experimental measurements for $12\leq Z\leq 33$. For normal operating conditions, using a LaB_6 filament, absorption of light element ($Z < 8$) X-rays in the specimen is important and has to be incorporated in the microanalysis. The validity of the K_{XSi} factors obtained have been confirmed by analysing two NBS glass standards of known composition and in recent research [20] related to composition stabilized polytypoids in the Al-O-N system. The relative simplicity of the EDXS microanalysis and the greater accuracy in the analysis when compared to the alternative EELS [21]

method makes this method very attractive, provided that the performance of the window is periodically monitored and careful measurements of K_{XSi} factors are carried out.

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Table 1

Material	Composition (wt percent)		Measured K_{XSi} Factors	
α-SiC[a,1]	C=30.0±0.34	Si=70.0±0.27	K_{CSi}=4.05	
β-SiC[a,1]	C=29.94±0.27	Si=70.07±0.21	K_{CSi}=3.98	
$TiC_{0.95}$[b,1]	C=20.06±0.28	Ti=79.94±0.26	K_{CSi}=3.97	K_{TiSi}=1.307
$VC_{0.88}$[b,1]	C=15.83±0.47	V=84.17±0.5	K_{CSi}=4.10	K_{VSi}=1.23
Si_3N_4	N=39.84±0.37	Si=60.16±0.28	K_{NSi}=3.3	
AlN[c,2]	N=34.20±0.29	Al=65.80±0.24	K_{NSi}=3.25	K_{AlSi}=0.95
SiO_2[a,1*]	O=52.91±0.12	Si=47.09±0.1	K_{OSi}=1.75	
MgO[a,1]	O=40.28±0.51	Mg=59.72±0.51	K_{OSi}=1.75	K_{MgSi}=0.92
Al_2O_3[a,1]	O=47.01±0.65	Al=52.99±0.49	K_{OSi}=1.75	K_{AlSi}=0.85
$MgAl_2O_4$[1]	O=45.5±0.25	Mg=16.98±0.11	K_{OSi}=1.75	K_{MgSi}=0.90
		Al=37.52±0.17		K_{AlSi}=0.90
FeS[d,3] (Troilite)	S=37.42±0.19	Fe=62.58±0.23	K_{SSi}=1.14	K_{FeSi}=1.40
GaAs[e,1]	Ga=48.86±0.79	As=51.14±0.83	K_{GaSi}=1.95	K_{AsSi}=2.20
TiO_2[a,1]	O=39.50±0.48	Ti=60.50±0.35	K_{OSi}=1.75	K_{TiSi}=1.307

a = International Monocrystals

b = Oak Ridge National Lab.

c = NEC Corporation, Japan

d = NASA Ames Laboratory

e = Bell Corporate Research

1 = single crystal, ion milled

2 = polycrystal, ion milled

3 = mineral, microtomed

4 = sputtered glass standard thin film

* = sample turns amorphous under the beam

Table 2

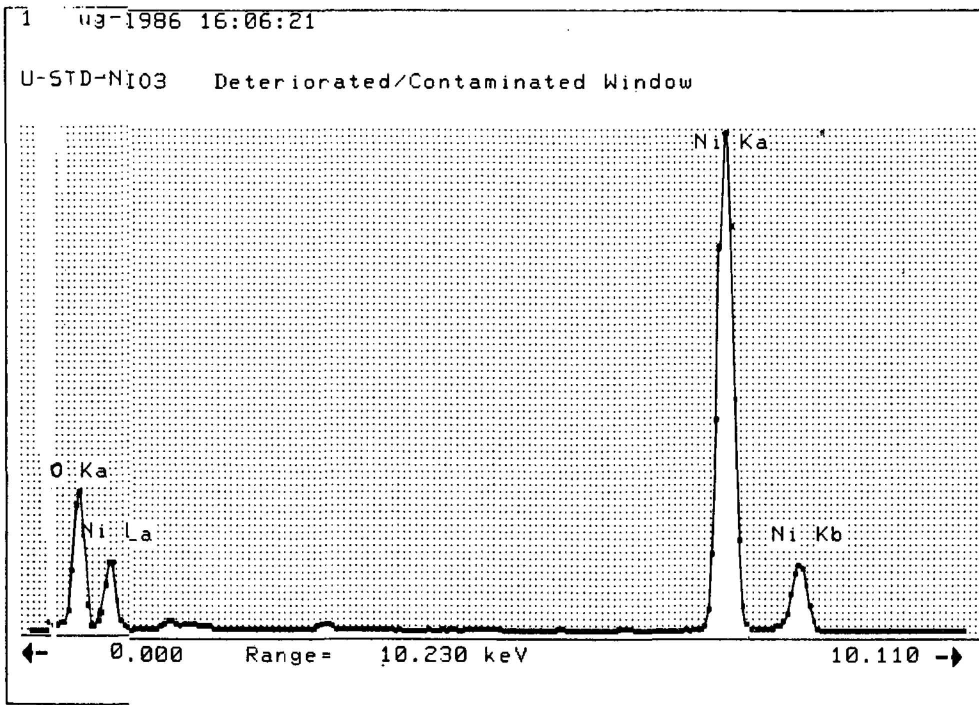
Composition (wt percent)

	K411		K412	
	NBS	NCEM	NBS	NCEM
O	42.36	43.85±0.25	43.57	44.01±0.34
Mg	8.85	8.64±0.08	11.66	11.19±0.13
Al		0.87±0.03	4.91	5.71±0.09
Si	25.38	23.90±0.14	21.20	22.28±0.19
S		0.37±0.03		
Ca	11.06	11.31±0.09	10.90	9.06±0.11
Fe	11.21	11.06±0.10	7.74	7.75±0.12

FIG. 1.--Representative energy dispersive X-ray spectra obtained from a NiO sample. Notice the degradation in the performance of the ultra-thin window detector, especially at the low energy regions, due to water vapour contamination.

FIG. 2.--Typical set of data obtained from a sample of AlN. The foil thickness at each data acquisition point (A,B,C,D) was measured by CBED. The points were chosen at multiples of the extinction distances (a), such that an internal consistency in the thickness measurements by CBED could be assured. However, the actual spectra were obtained in a non-Bragg condition (b) to avoid any channelling effects.

FIG. 3.--Summary of K-factor data. Our measurements are compared with those of Thomas (1985) and Cliff et al. (1984). The continuous curve is calculated for the best estimated detector parameters (inset) using the mass absorption coefficients of Zaluzec (1984).



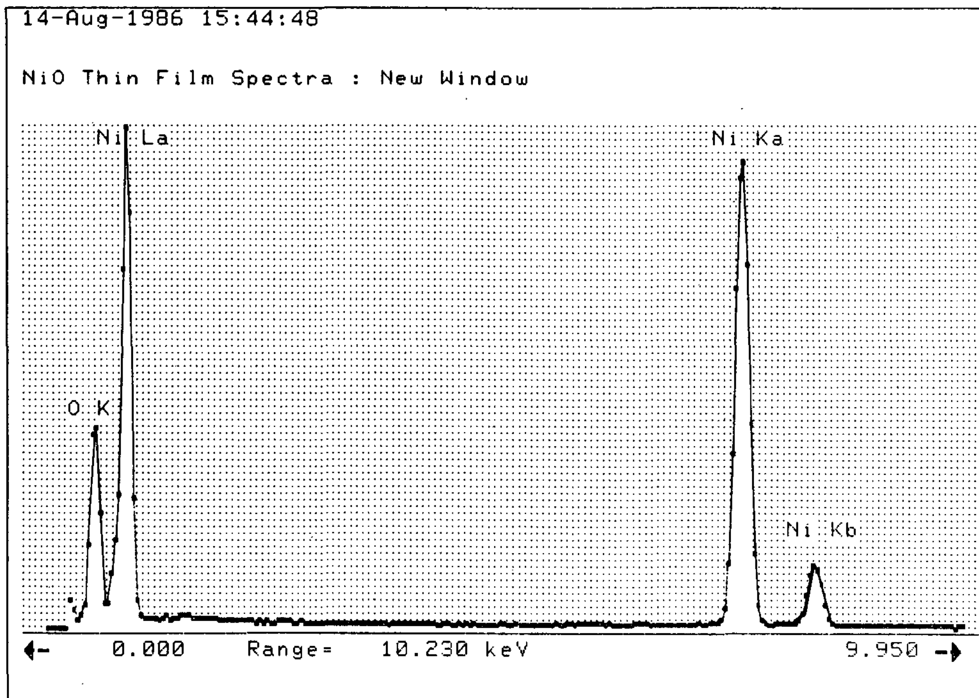


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Fig. 1

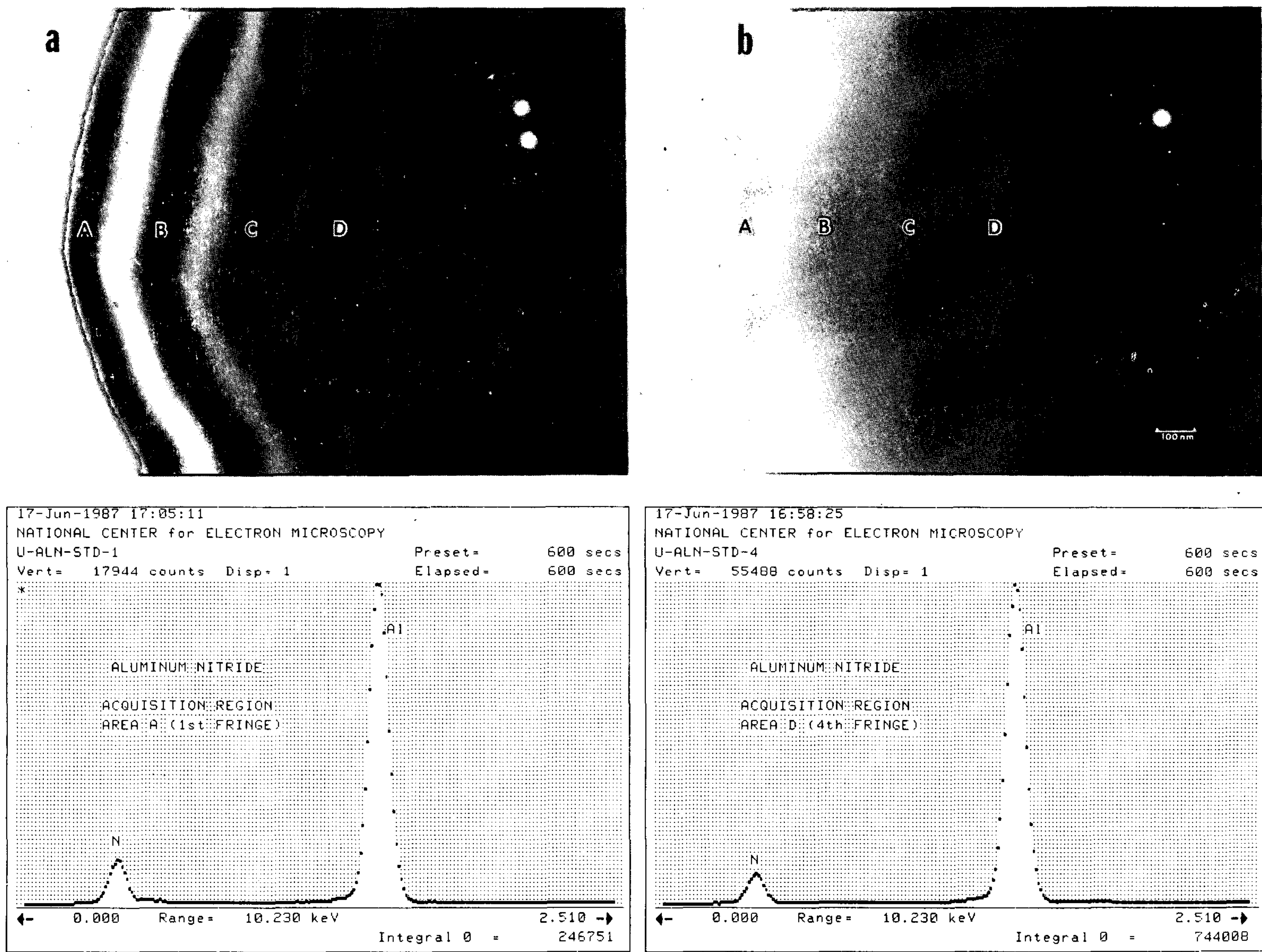

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Fig. 2

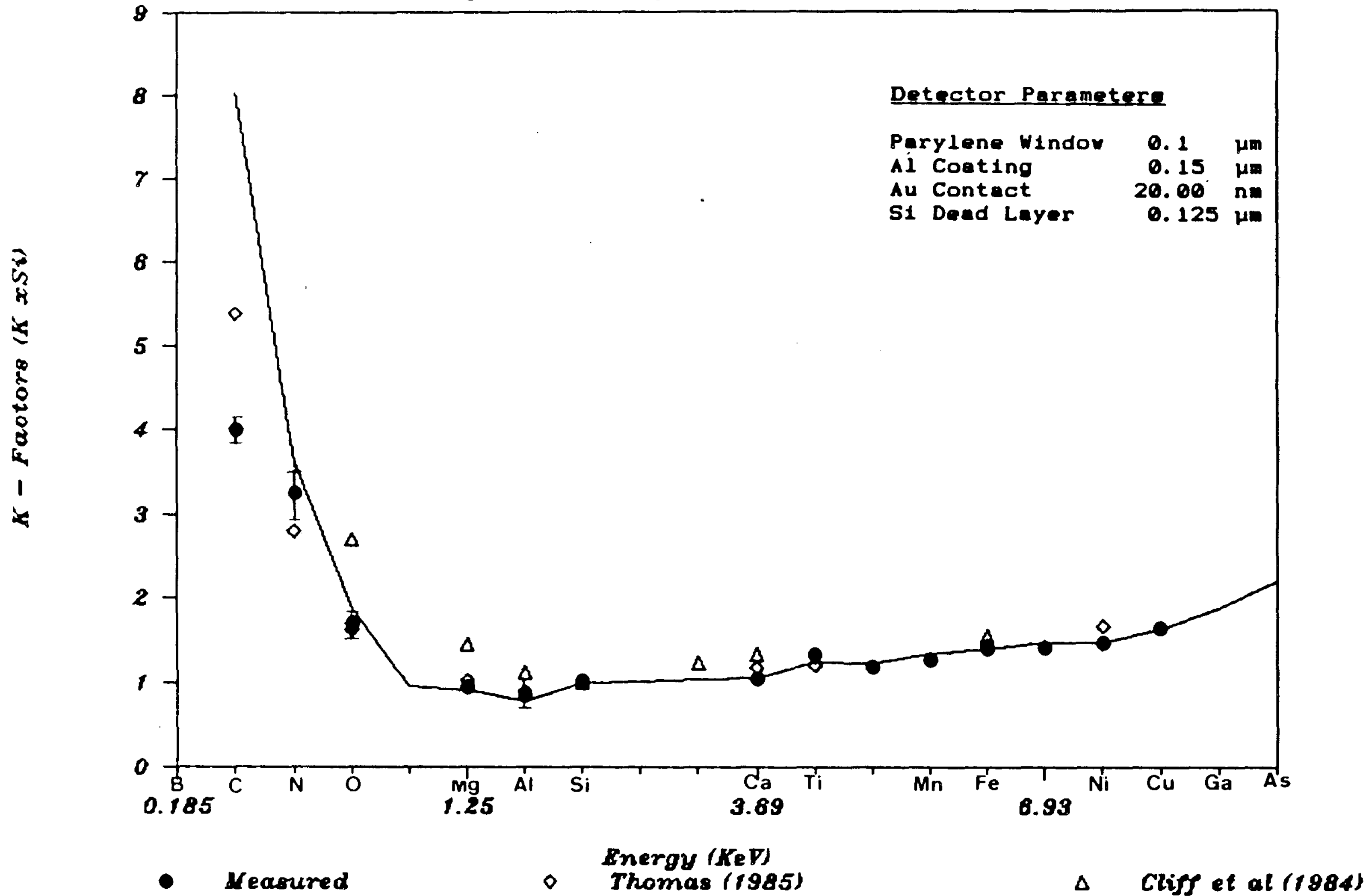

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Fig. 3

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