X-RAY AND ABSORPTION WAVELENGTHS AND TWO-THETA TABLES

SECOND EDITION

Prepared by

E. W. WHITE

G. G. JOHNSON, JR.

ASTM Data Series DS 37A

AMERICAN SOCIETY FOR TESTING AND MATERIALS

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Sponsored by

ASTM Committee E-2
on Emission Spectroscopy

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Foreword

X-ray emission spectrography (X-ray fluorescence) and the electron microprobe are two basic techniques for elemental chemical analysis. X-ray fluorescence instruments are now used routinely for the determination of all elements fluorine and heavier. The more efficient X-ray excitation by electrons used in the microprobe makes it feasible to work with all elements boron and heavier. Lithium and beryllium also can be detected in the microprobe although not as readily as the heavier elements. Fundamental to the successful use of these techniques is the proper application of X-ray emission line and absorption edge wavelength data, together with calculated values for the Bragg diffraction angles of the analyzing crystals. The trend is toward the analysis of specimens having increasing complex chemistry as well as toward utilization of X-ray emission line shifts (soft X-ray spectroscopy) to determine how elements are chemically bonded in a given specimen. These developments have created a need for reference tables in convenient form. This volume is the second edition of such tables. It provides a listing of all X-ray emission lines (160 Å* and shorter), incorporating some 3400 first order lines, absorption edges, and the calculated two-theta values for 23 commonly used analyzing crystals.

Since publication of the first edition as ASTM Data Series DS 37, *X-Ray Emission Line Wavelength and Two-Theta Tables* in 1965, [*1*][1] several developments have stimulated preparation of a new edition. Taken singly, perhaps none of these developments would warrant a new edition, but together they represent a major advancement over the earlier version.

New analyzing crystals are being developed continually. The most important recent advances have been made with materials that are not single crystals in the usual sense. These include increased use of the so-called pseudo-crystals or Langmuir-Blodgett preparations of soap films. Lead stearate continues to be the most commonly used pseudo-crystal, although the laurates and lignocerates are now commonly used also. The newly developed synthetic graphite sold by Union Carbide under the trade name "Ucar" [*2*] may be the precursor to an important new family of analyzing materials. This graphite is really a highly oriented polycrystalline material giving a rather broad rocking curve ($\sim$0.4 deg), but its very high reflection efficiency more than offsets this limitation for many applications. Clinochlore is now in extensive use—especially in microprobe applications where it is suited ideally to the analysis of oxygen [*3*]. Its mechanical and chemical stability are particularly useful in soft X-ray applications. Another trend in analyzer crystal usage is to employ more than one orientation of the same crystal. This has become especially popular for LiF, ADP, EDDT, and quartz.

The X-ray line designations and column headings have been rendered much more readable in this edition, thanks to the availability of a special IBM print train. This train, owned by the Joint Committee on Powder Diffraction Standards, carries most of the Greek letters as well as large and small type, upper and lower case, and prime characters. As a result the table has the appearance of being printed from set type.

The situation with regard to satellite lines has been reviewed extensively. It was decided to delete most of the satellite lines given in DS-37 from this table. The reason is that apparently most of them were identified originally from X-ray films in which they were recognized as undulations in intensity within emission bands or broad wavelength tails. The identification of many of them as real satellite lines is now in doubt.

Correctional formulas are being used more and more in quantitative X-ray fluorescence and electron microprobe analysis. Fundamental to all these correctional formulas is knowledge of the X-ray absorption edge wavelength (energies) for each of the elements in a given matrix. Tabulations of absorption edges are usually quite separate from the emission line wavelength tables. This edition integrates the absorption edges in a manner that makes them quite easily retrieved.

This wavelength table has been compiled with the use of high resolution spectrometers in mind. It is realized that for many spectrometers, not all of the lines listed will be resolved; but it is believed better to have the lines listed, although unresolved, than to have the lines resolved and go unidentified or even misidentified.

The chemical effect on X-ray spectra is now common knowledge among X-ray fluorescence and microprobe users. It is observed as changes in line wavelength, shape, and relative intensity. The wavelength shift is strongest for the light element K-lines. Because the K-line peak shifts are often quite large they must be taken into account when "peaking" the spectrometer for even routine analysis. For this reason, one column (Δ) has been used in this table to designate the

[1]The italic numbers in brackets refer to the list of references appended to this Foreword.

magnitude of shift that one might encounter for the K-series lines. This will be useful in deciding whether or not one needs to repeak the spectrometer during intensity measurement of a given set of standards and unknowns.

It is impossible to assign accurate relative intensity values to X-ray lines even within a given series (K, L, M, etc.) of a given element. The reason is that observed relative intensities are dependent upon a host of experimental parameters including: energy of the X-rays or electrons causing the excitation; self-absorption within the sample; wavelength-dependent response or efficiency of the crystal and detector. The self-absorption effect is the primary basis for the observed chemical effect among the L-series lines. The $L\alpha$ to $L\beta$ line intensity ratio may vary by a factor of two to five, depending on the element and experimental conditions used. Nevertheless, it is important to know whether a given line can be expected to be seen as quite strong, weak, or very weak. Extensive search of the literature failed to provide us with enough information to assign such values for this table. The only recourse was to experimentally collect the required data. This was done using an Applied Research Laboratories Model EMX microprobe. The results of dozens of spectral scans (K, L, and M Series) have gone into arriving at the values used in this compilation. The major exception to this is with regard to the relative intensities among the third period element K-series where we have used mostly the relative intensity from several publications of Baun and Fischer. Most published 2θ tables have used a constant set of relative L-series intensities for all elements. However, there are quite drastic changes with increasing atomic number, and they have been taken into account here. Relative intensities have been determined for the M-series lines. No attempt has been made to assign N-series line intensities as these are seldom used analytical lines and we were unable to experimentally measure N spectral series.

No attempt has been made to include an index of refraction correction. All wavelengths are given in units of Å* as introduced by Bearden [*4*].

Data in the second portion of this book, as in the earlier edition, is ordered on the basis of increasing wavelength. This arrangement makes possible the phasing in and out of crystals during just their useful λ range. This allows compilation of 2θ value for a total of 23 analyzing crystals. Such a phasing is, of course, not feasible in the first section where the data are ordered primarily on the basis of increasing atomic number.

Description of Table

The table is divided into two major sections separated by a periodic chart showing the major lines of each element.

The first section presents all wavelength lines and X-ray absorption edges shorter than 160 Å*. Data in this section are listed on the basis of atomic number ($Z = 3 \rightarrow 98$) with decreasing λ within each element. The two-theta values are shown for a selection of the 15 most commonly uscd analyzing crystals.

The second section gives all the lines shown in the first section arranged on the basis of increasing wavelength. Lines having a relative intensity of 1.0 or less are carried only to the third order. The more intense lines are carried to a maximum of the tenth order or until $n\lambda$ exceeds 160 Å.*

The column headings and explanation of the symbols used within each column are as follows:

The two columns under the heading *El* show the accepted chemical symbol for each element.

The *Line* designation usually gives the Siegbahn notation ($K\alpha$, $L\beta$, etc.), but when that is not established then the level designations are used to show the two levels involved in the transitions.

The comment column (*c*) carries certain comments according to the following key:

	/ or C	R	*	$
A				X
B			X	
C			X	X
D		X		
E		X		X
F		X	X	
G		X	X	X
H	X			
I	X			X
J	X		X	
K	X		X	X
L	X	X		
M	X	X		X
N	X	X	X	
O	X	X	X	X

where:

/ indicates value was interpolated from data for neighboring elements.

C indicates value was calculated from other transitions for the same element.

R indicates that the "best" measured value was rejected by Bearden and Burr in their least-squares energy level adjustment. Hence the original value has been replaced by the adjusted value obtained by Bearden and Burr.

* indicates that this line does *not* represent a dipole transition and hence will be usually quite weak.

$ denotes a transition in which the electron in the initial state occupies a level that is unoccupied in the ground state of the isolated atom. These lines have been called "semi-optical" lines and were so designated in X-Ray Wavelengths. However, since the experimentally observed radiation comes from a solid target (in some cases, a chemical compound rather than a pure element), the transitions can be attributed mainly to solid state or chemical effects or both.

The *N* column denotes the diffraction order from the Bragg equation,

$$n\lambda = 2d \sin\theta.$$

The *I* or relative intensity column indicates the relative intensity of a given line, within a given series for a given element and order of diffraction. Obviously the actual intensity will vary from order to order in a manner dictated primarily by the structure factors of a given crystal and orientation. Occasional intensities left blank indicate that the intensity is very weak and unknown. The unresolved $K\alpha_1\alpha_2$ line intensity is given as 150, or the integrated intensity of the lines.

Z is the numerical value for the atomic number.

The value for *R* is the primary literature source according to the following key:

R = 0, the reference is Cauchois [5] where the wavelength was in kX units.

R = 1, the reference is Cauchois [5] where the wavelength was in Å units.

R = 6, the reference is Bearden [6] where the wavelength is in Å* units.

The *KeV* value was determined by dividing the wavelength of each line (first order) or absorption edge into the value for $h\nu$.

$$\text{ex.:} \quad \text{KeV} = \frac{12.396}{\lambda \text{Å}^*}$$

Lambda is wavelength in Å*. Wavelengths which appear as 31.599999, for example, should be understood to be 31.6. The series of 9s is due to the finite word length and numerical representation of certain numbers on a binary computer.

P is precision of data given in terms of 10^{-}. This figure represents the number of significant digits to the right of the decimal point in the *Lambda* column.

Δ is given only for the K-series lines where applicable. Also given in terms of 10^{-}.

Table 1 summarizes the pertinent data about each crystal used in generation of the 2θ values as tabulated. Silicon (111) and germanium (111) both give zero intensity second order diffraction. For that reason, 2θ values for all second order diffractions for these crystals have been generated as blanks.

TABLE 1—*The 23 analyzing crystals used to develop the two-theta data.*

Crystal Designation	Crystal Name	Bragg Diffraction Indices, hkℓ	2d Å*
Lmel	Lead melissate	Film	160.
Llign	Lead lignocerate	Film	130.
Lstear	Lead stearate	Film	100.7
Llaur	Lead laurate	Film	70.
Chlor	Clinochlore	001	28.392
KAP	Potassium acid phthlate	100	26.632
RbAP	Rubidium acid phthlate	100	26.121
Mica	Muscovite	002	19.840
Gypm	Gypsum	020	15.19
ADP	Ammonium dihydrogen phosphate	101	10.64
EDDT	Ethylenediamine D-tartrate	020	8.808
PET	Pentaerythritol	002	8.742
Qtz	α-Quartz	100	8.52
ADP	Ammonium dihydrogen phosphate	200	7.50
Graph	Graphite (also 101 α-Quartz)	002	6.708
Ge	Germanium	111	6.532
Si	Silicon	111	6.2709
ADP	Ammonium dihydrogen phosphate	112	6.14
NaCl	Sodium chloride	200	5.6410
LiF	Lithium fluoride	200	4.0267
LiF	Lithium fluoride	220	2.848
Qtz	α-Quartz	203	2.7490
Topaz	Topaz	303	2.7120

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[*5*] Cauchois, Y. and Hulubei, H., *Constantes Selectionnees Longuers d'onde des Emissions X et d'Absorption X,* Hermann & Cie, Editeurs, Paris, 1947.

[*6*] Basic data as presented in Ref 4, with minor revisions and supplied by J. A. Bearden, June 1969 on punched IBM cards.