UNCLASSIFIED

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349853 3

ORNL-1917
Chemistry 5

A STUDY OF X-RAY FLUORESCENCE FOR THE ANALYSIS OF RARE EARTHS AND OTHER COMPLEX GROUPS

H. W. Dunn

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

UNCLASSIFIED

UNCLASSIFIED

ORNL-1917

Copy No. 3

A STUDY OF X-RAY FLUORESCENCE FOR THE ANALYSIS OF RARE EARTHS AND OTHER COMPLEX GROUPS

H. W. Dunn

June 7, 1955

DATE ISSUED

JUL 13 1955

STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION
C. P. Keim, Director

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Oak Ridge, Tennessee

Contract No. W-7405-eng-26

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0349853 3

UNCLASSIFIED

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-11. Laboratory Records Department
12. Laboratory Records, ORNL R. C.
13. C. E. Larson
14. L. B. Emlet (K-25)
15. J. P. Murray (Y-12)
16. A. M. Weinberg
17. E. H. Taylor
18. G. E. Boyd
19. J. A. Swartout
20. E. D. Shipley
21. C. P. Keim
22. W. H. Jordan
23. F. C. VonderLage
24. S. C. Lind
25. F. L. Culler
26. A. H. Snell
27. A. Hollaender
28. M. T. Kelley
29. C. D. Susano
30. G. H. Clewett
31. W. R. Grimes
32. K. B. Brown
33. K. Z. Morgan
34. K. A. Kraus
35. J. H. Frye, Jr.
36. C. E. Normand
37. L. O. Love
38. R. S. Livingston
39. T. A. Lincoln
40. A. S. Householder
41. C. S. Harrill
42. C. E. Winters
43. D. W. Cardwell
44. E. M. King
45. A. J. Miller
46. D. D. Cowen
47. J. A. Lane
48. M. J. Skinner
49. Russell Baldock
50. P. S. Baker
51. Boyd Weaver
52. S. J. Cromer
53. J. R. McNally, Jr.
54-58. H. W. Dunn
59. W. F. Peed
60. F. N. Bensey (K-25)

EXTERNAL DISTRIBUTION

61. R. F. Bacher, California Institute of Technology
62. D. F. Cope, AEC, ORO
63. Division of Research and Medicine, AEC, ORO
64-359. Given distribution as shown in TID-4500, under Chemistry category.

DISTRIBUTION PAGE TO BE REMOVED IF REPORT IS GIVEN PUBLIC DISTRIBUTION

ABSTRACT

This report demonstrates the complexity of analysis of rare earth and fourth period elements by x-ray fluorescence and gives an estimation of the magnitude of the interferences due to excitation and absorption.

A STUDY OF X-RAY FLUORESCENCE FOR THE ANALYSIS OF RARE EARTHS AND OTHER COMPLEX GROUPS

H. W. Dunn

INTRODUCTION

This is a report on the feasibility of accurate analysis of rare earth separation products by means of X-ray fluorescence and a study of the nature and magnitude of the interferences in both the rare earth series and in complex mixtures of fourth period elements. Previous work in this laboratory demonstrated the practicality of X-ray fluorescence analysis of zirconium oxide in a uranium oxide matrix[1] and X-ray absorption analysis for uranium in liquid samples[2].

Work on the analysis of rare earths by X-ray fluorescence was done in 1947 by Clark, Wagner and Carley[3] and recently by Salmon and Blacklodge[4]. Neither group investigated the problem far enough to determine if accurate quantitative analysis for the rare earth elements could be obtained by X-ray fluorescence. Friedman and Birks[5] give a good discussion of X-ray fluorescence equipment and discuss briefly some interferences that will be found. Beattie and Brissey[6] describe an approximate method of correcting mathematically for interferences from other elements. This method does not reliably correct for the interferences and might be expected to be less applicable to the rare earths and other complex series.

PRELIMINARY

The "L" lines of the rare earth elements, which require excitation voltages of about 10,000 volts, were used as the General Electric XRD-3 available voltage of 50,000 volts is not adequate to excite efficiently the "K" lines of these elements. The wave length of the "L" lines of the rare earth elements are listed by Cauchois and Hulubei[7]. From this data and the crystal spacing of the mica crystal on the X-ray fluorescence analyzer, the 2θ position of each line is readily calculated using the Bragg formula

$$n\lambda = 2\ d\ \mathrm{Sin}\ \theta.$$

The approximate resolution of the X-ray fluorescence analyzer on the XRD-3 was determined by measuring the line widths from a scan of the samarium "L" spectrum. Most lines 0.5° apart and very strong lines 0.75° apart gave no detectable interference. Using these data and the relative intensities of X-ray emission lines as given by Compton and Allison[8], lines useful for analysis were selected and interferences anticipated. Table I lists the lines most useful for direct analysis of the constituent rare earth elements and the interfering lines of each.

Pure samples of samarium, gadolinium, terbium, erbium, ytterbium, yttrium and chromium oxides and an eighty per cent dysprosium oxide sample were obtained from the Isotope Chemistry group of the Stable Isotopes Research and Production Division. Since yttrium is present in most of the routine samples, its analysis is also desired. Chromium was chosen as an internal standard because the wave length of the Cr $K\alpha$ lines is as near that of the "L" lines of the rare earth elements as can be obtained without having line interferences. (La is not present in any of the samples received by this laboratory. If it were in future samples, corrections would have to be made to the Cr $K\alpha$ line intensity.)

TABLE I

RARE EARTH ELEMENT LINES

Element	Line	Wave Length in X Units*	Interference
Cr	$K\alpha$	2286.30	La $L\beta_{10}$ La $L_I\beta_9$ La $L\beta_2$
La	$L\alpha_1$	2659.7	None
Ce	$L\alpha_1$	2556.0	None
Pr	$L\alpha_1$	2457.7	La $L\beta_1$
	$L\beta_1$	2253.9	None
Nd	$L\alpha_1$	2365.3	La $L\beta_6$
	$L\beta_1$	2162.2	None
Sm	$L\alpha_1$	2195.0	Ce $L\beta_2$
	$L\beta_1$	1993.6	Tb $L\alpha_2$
Eu	$L\alpha_1$	2116.3	Pr $L\beta_2$
	$L\beta_1$	1916.3	Dy $L\alpha_2$
Gd	$L\alpha_1$	2041.9	La $L\gamma_2$ La $L\gamma_3$ Ce $L\gamma_1$ Nd $L\beta_2$
	$L\beta_1$	1842.5	Ho $L\alpha_1$
Tb	$L\alpha_1$	1971.5	Sm $L\beta_3$
Dy	$L\alpha_1$	1904.90	Eu $L\beta_1$
Ho	$L\alpha_1$	1841.0	Gd $L\beta_1$
	$L\beta_2$	1563.7	Er $L\beta_6$
Er	$L\alpha_1$	1780.68	Tb $L\beta_1$ Tb $L\beta_4$
	$L\beta_1$	1584.09	Gd $L\gamma_1$ Eu $L\gamma_3$

Relative Line Intensities**			
$L\alpha_1$	100	$L\beta_1$	51.0
$L\beta_2$	20	$L\alpha_2$	11.0
$L\gamma_1$	10	$L\beta_3$	6.8
$L\beta_4$	5.4	$L\gamma_3$	2.3
$L\gamma_2$	1.7	$L\beta_6$	1.0
$L\beta_9$	0.5	$L\beta_{10}$	0.5

* Cauchois and Hulubei[6]

** Compton and Allison[7]

TABLE I
(continued)

Element	Line	Wave Length in X Units	Interference				
Tm	$L\alpha_1$	1722.8	Sm $L\gamma_1$	Dy $L\beta_4$	Dy $L\beta_1$		
	$L\gamma_1$	1312.7	Er $L\gamma_3$	Er $L\gamma_2$			
Yb	$L\alpha_1$	1668.50	Tb $L\beta_2$	Dy $L\beta_3$	Y $K\alpha_2^2$	Sm $L\gamma_2$	Ho $L\beta_4$
	$L\gamma_1$	1264.99	Tm $L\gamma_3$	Tm $L\gamma_2$			
Lu	$L\alpha_1$	1616.17	Dy $L\beta_2$	Ho $L\beta_3$			
	$L\gamma_1$	1219.74	Yb $L\gamma_3$	Yb $L\gamma_2$			
Y	$K\alpha$	828.52	None				

EXPERIMENTAL

Previous analytical studies by this laboratory were made with the General Electric XRD-3 with revised counting equipment using a proportional counter and extra scalers[2]. However, due to the extremely soft radiation encountered in this rare earth problem it was found desirable to use the original Geiger-Mueller counter because of the reduced background.

Pressed buttons for use in the XRD-3 were prepared by grinding 0.250 gram of rare earth oxide and 0.250 gram of Cr_2O_3 with 1.000 gram of ordinary corn starch, then pressing into a button 1-1/8 inch in diameter at 8000 psi. Other buttons containing from 0.0025 to 0.250 gram of rare earth oxide ground with 0.250 gram of Cr_2O_3 and 1.000 gram of corn starch were prepared to simulate various percentages of the rare earth element from 1 per cent to 100 per cent. (Errors due to reduced self-absorption and scattering effects in these buttons are discussed later.)

Line intensities were determined by scaling out a pre-set number of counts at the peak of each line used in the analysis; from the measured time interval and the number of counts the counting rate was obtained. For most rare earth samples the counting rate for the 0.250 gram of the pure rare earth oxide was less than 200 counts per second and for the 0.250 gram of the chromium oxide was less than 250 counts per second. It was necessary to correct for background count for those elements which were present in low abundance as the counting rate is then only slightly above the background count. To obtain the background correction at each line, the background intensity was taken for several buttons containing one rare earth element each at points where no lines were present. (If several rare earth elements are present, it is difficult to find a spectral

region completely free of lines.) Although all the buttons do not show the same background, they do show a definite background trend; hence, it is possible to take a background reading on actual samples at some wave length that is free of lines and then correct each line for the background count, $B\lambda$, expected at that wave length by use of the correction factor determined for the sample button. As $B\lambda$ for an individual button varies somewhat, this value may be off as much as 0.5 count per second out of a possible 2 to 4 counts per second background.

Considering the spectographic analysis of the major constituents in the mica crystal (Table II), the presence of chromium, the internal standard, and the ratios obtained for the pure rare earth elements and rare earth samples for which the analysis was known, the graph (Figure 1) was drawn to give the location of the lines on the working curves (Figure 2) for the rare earth elements for which no standards were available.

The working curves were prepared by plotting on log paper the percentage of rare earth oxide as ordinate and the ratio of the intensity of the rare earth line to the Chromium $K\alpha$ lines as the abscissa for each of the rare earth and yttrium lines that were to be used for analysis. Data for this graph were obtained from the pure samples described above, from rare earth samples for which the analysis was known and from the graph (Figure 1). The points representing the various percentages of each element were connected as nearly as possible by a straight line (see Figure 2). By checking with rare earth samples analyzed by the emission spectrographic procedure[9], these working curves were found to be reasonably accurate (see Table III). Figure 2 shows some anomalies in line positions which can be associated with the complexity of the absorption and excitation of the X-ray fluorescence spectrum as discussed by von Hevesy[10] and Compton and Allison[8].

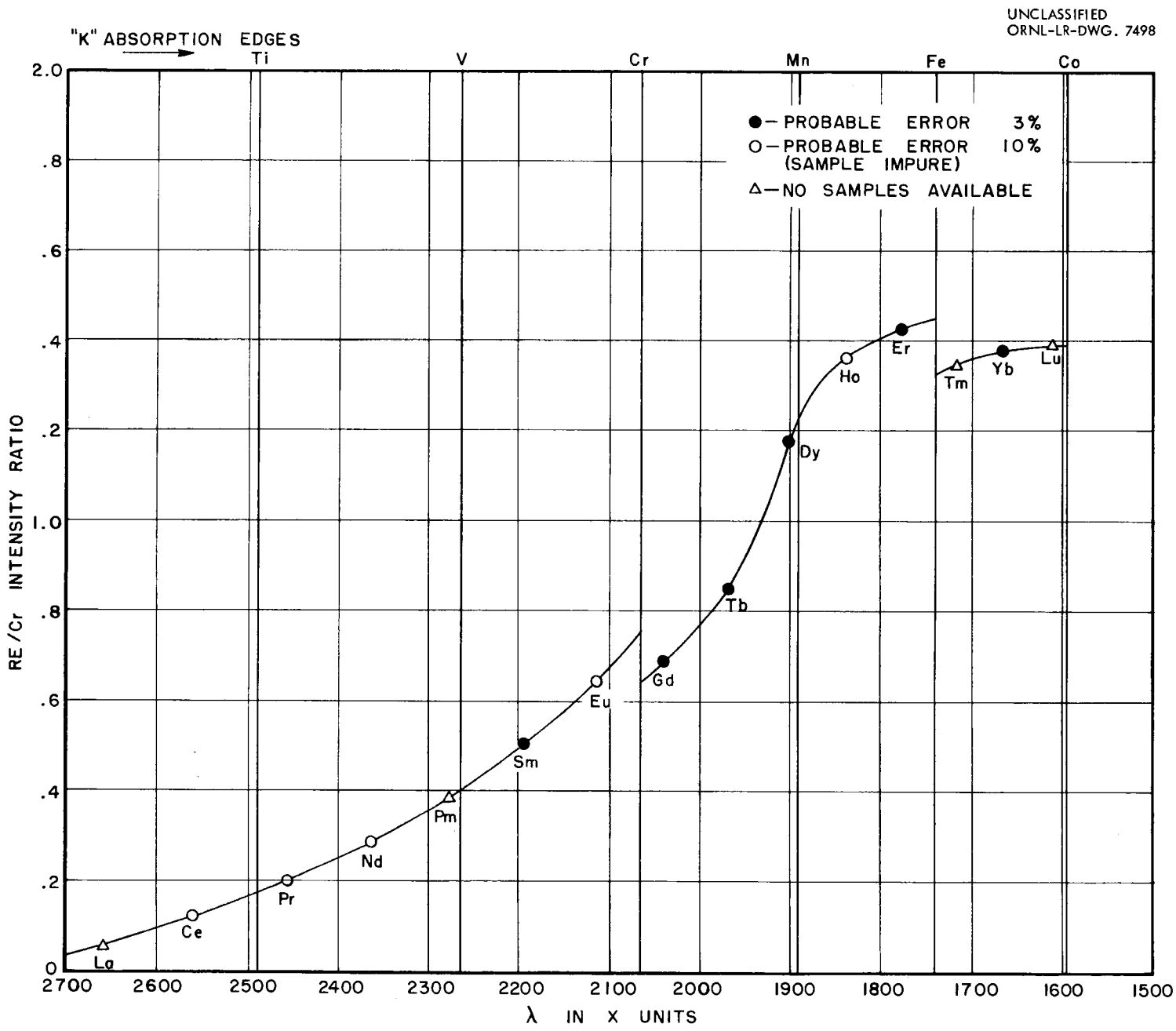

FIGURE 1. RARE EARTH / CHROMIUM RATIO VERSUS WAVELENGTH OF RARE EARTH L_{α_1} LINE

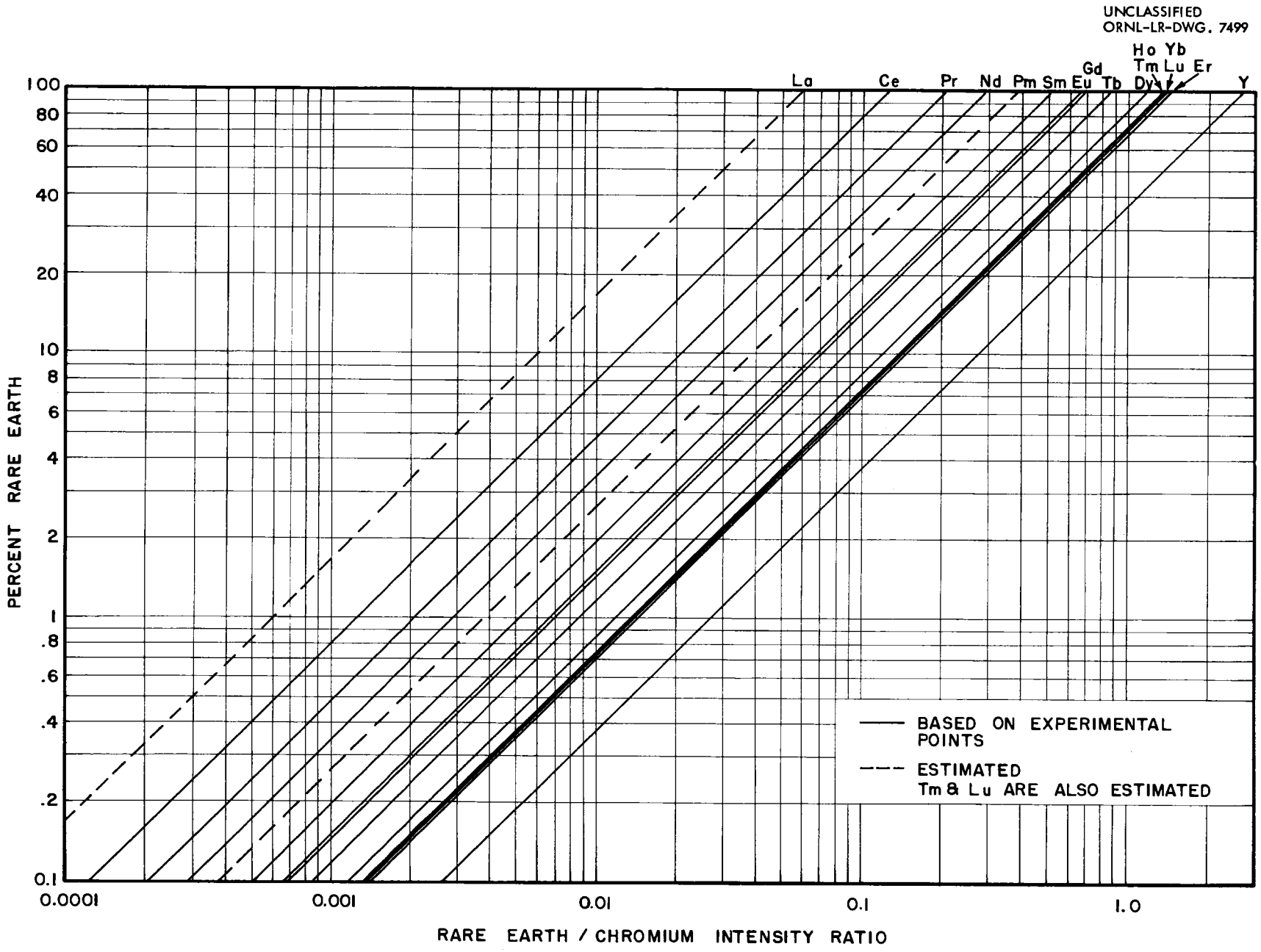

FIGURE 2. WORKING CURVES FOR $L\alpha_1$ LINES OF RARE EARTHS AND $K\alpha$ LINES OF CHROMIUM AND YTTRIUM

TABLE II

SPECTOGRAPHIC REPORT ON MICA CRYSTAL USED ON THE XRD-3

Values in Per Cent

Al	> 5.00
Ba	0.05
Cr	0.05
Fe	3.00
Mg	2.00
Mn	0.05
Na	1.30
Si	> 10.00
Ti	0.20

TABLE III

COMPARISON OF RARE EARTH DATA

	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
No. 32SC										
X-Ray		0.5	0.2	2.5	88.0	6.0	0.3			
Spectographic		---	---	3.8	88.0	4.8	0.4			
Difference		0.5	0.2	-1.3	0.0	1.2	-0.1			
No. 32AC										
X-Ray	0.2	0.5	3.4	24.0	70.0	0.4				
Spectographic	---	---	3.7	26.0	72.0	0.7				
Difference	0.2	0.5	-0.3	-2.0	-2.0	-0.3				
No. 55										
X-Ray		0.8	2.9	33.5	60.0	1.5				
Spectographic		---	3.0	31.0	60.0	<1.0				
Difference		0.8	-0.1	2.5	0.0	---				
No. 55Y										
X-Ray		0.4	2.2	20.4	37.8					
Spectographic		---	1.8	18.6	36.0					
Difference		0.4	0.4	1.8	1.2					
No. ADM										
X-Ray	3.3	0.6	2.8	1.0	4.5	1.3	3.3	0.3	1.3	21
Spectographic	3.1	<1.0	2.8	1.3	3.8	PW*	2.8	---	---	22
Difference	0.2	0.0	0.0	-0.3	0.7	0.0	0.5	0.3	1.3	-1
No. 6810Y										
X-Ray	30	0.5	14.5		21.2					35
Spectographic	30	<1.0	10.0		?					?
Difference	0	0.0	4.5		---					--

* Present, weak.

INTERFERENCE EFFECTS

Other than direct line interferences, the chief interferences to be expected in the X-ray fluorescence spectrum arise from absorption and excitation. The absorption interference may be of two principal types, general mass absorption effects and absorption edge effects. For example, when two element lines some distance apart are used, a third element will absorb the X-ray fluorescence line radiation having the longer wave length to a greater extent, since $\mu = k\lambda^3 Z^4$, thereby causing a change in the intensity ratio. The farther apart the two lines are the more pronounced the effect. If the third element has an absorption edge occuring between two lines, a more serious effect occurs in that the line having the shorter wave length is absorbed to a greater extent than the other provided the lines are not too far apart since $\mu' = k'\lambda^3 Z^4$ and $k' > k$. Such edge effects should be evaluated for each group.

There are also two main types of excitation interference effects which affect the intensity ratio: one, when the excitation radiation due to the fluorescence line radiation from a third element falls between the absorption edges of the two elements being measured, and the other, when this radiation is located on the short wave length side of the absorption edges of both elements but close to the one with the shorter wave length. When the exciting fluorescence radiation falls between the absorption edges of the two elements being measured, the line radiation from the element of longer λ edge will be excited but not the line radiation from that of the shorter λ edge thereby changing the intensity ratio of the lines under comparison. If the third element has an X-ray emission line on the short wave length side of the absorption edges of both elements, this radiation will affect the one having the closer absorption edge to a greater extent again changing the intensity

ratio of the element lines. Another excitation effect that is very similar to fluorescence line radiation effects from a third element is the characteristic line radiation from the X-ray target. This will produce essentially the same effects as excitation effects of a third element. By choosing the proper X-ray target and excitation conditions, this effect can be reduced or eliminated. In addition to all these individual interferences, there can also be various combinations of effects of this nature.

The equations developed by Beattie and Brissey[6] give some improvement in the data for some simple systems, but fail to correct for interferences in more complex systems as well as in some simple systems. This failure is mainly due to the lack of correction for excitation effects and the difficulty in obtaining good values for the absorption coefficients for complex mixtures.

RARE EARTH DATA AND DISCUSSION

In Figure 2 there is an anomalous shift between the europium and gadolinium lines on the working curves. The "K" absorption edge of chromium (the internal standard) is between europium and gadolinium with the gadolinium $L\alpha_1$ line being on the short wave length side of the "K" absorption edge of chromium thereby being absorbed to a much greater extent than the europium $L\alpha_1$. In addition, the gadolinium $L\alpha_1$ line excites the chromium "K" spectrum strongly while the europium $L\alpha_1$ line does not. These effects probably account for the anomaly at this point. This same situation applies to other rare earth elements in that the $L\alpha_1$ line radiation of gadolinium and those above is absorbed to a greater extent than the $L\alpha_1$ line radiation of europium and those below. Also the $L\alpha_1$ line radiation of gadolinium and those above will excite the chromium "K" spectrum while

the $L\alpha_1$ line radiation of europium and those below will not.

There is another anomalous shift between erbium and thulium. Since the "K" absorption edge of iron is between the $L\alpha_1$ line radiation of these two elements it will absorb the $L\alpha_1$ line radiation of thulium to a greater extent than the $L\alpha_1$ line radiation of erbium. The mica crystal contains about three per cent iron which probably accounts for the erbium and thulium anomaly.

Figure 3 shows the graph obtained by diluting the rare earths to simulate various percentages of the rare earth elements from 1 to 100 per cent. The samarium line slope differs markedly from the others presumably because samarium is on the more transparent side of the absorption edge of the reference chromium while the others are on the more opaque side of this absorption edge. Also, the slopes of all these lines differ from the slopes of the lines in Figure 2. The lines in Figure 2 are based on buttons having a constant mass while the buttons used for Figure 3 had the total mass decreasing as the percentage of rare earth decreased. With gadolinium, dysprosium, erbium and ytterbium the slopes increase as the atomic number increases. This probably is accounted for by the fact that the gadolinium $L\alpha_1$ line is very close to the opaque side of the chromium "K" absorption edge where the $L\alpha_1$ line radiation is absorbed very efficiently. As the percentage of gadolinium decreases, this becomes even more pronounced. As the atomic number of the rare earth element increases, the wave length of the $L\alpha_1$ line radiation gets farther from the opaque side of the chromium "K" absorption edge, the absorption becomes less efficient and the line on the graph becomes steeper. This effect is decreased some by the fact that the $L\alpha_1$ line radiation of these elements excite the chromium "K" spectrum. In addition, as the percentage of rare earth decreases, the radiation from the target is absorbed

UNCLASSIFIED
ORNL-LR-DWG. 7500

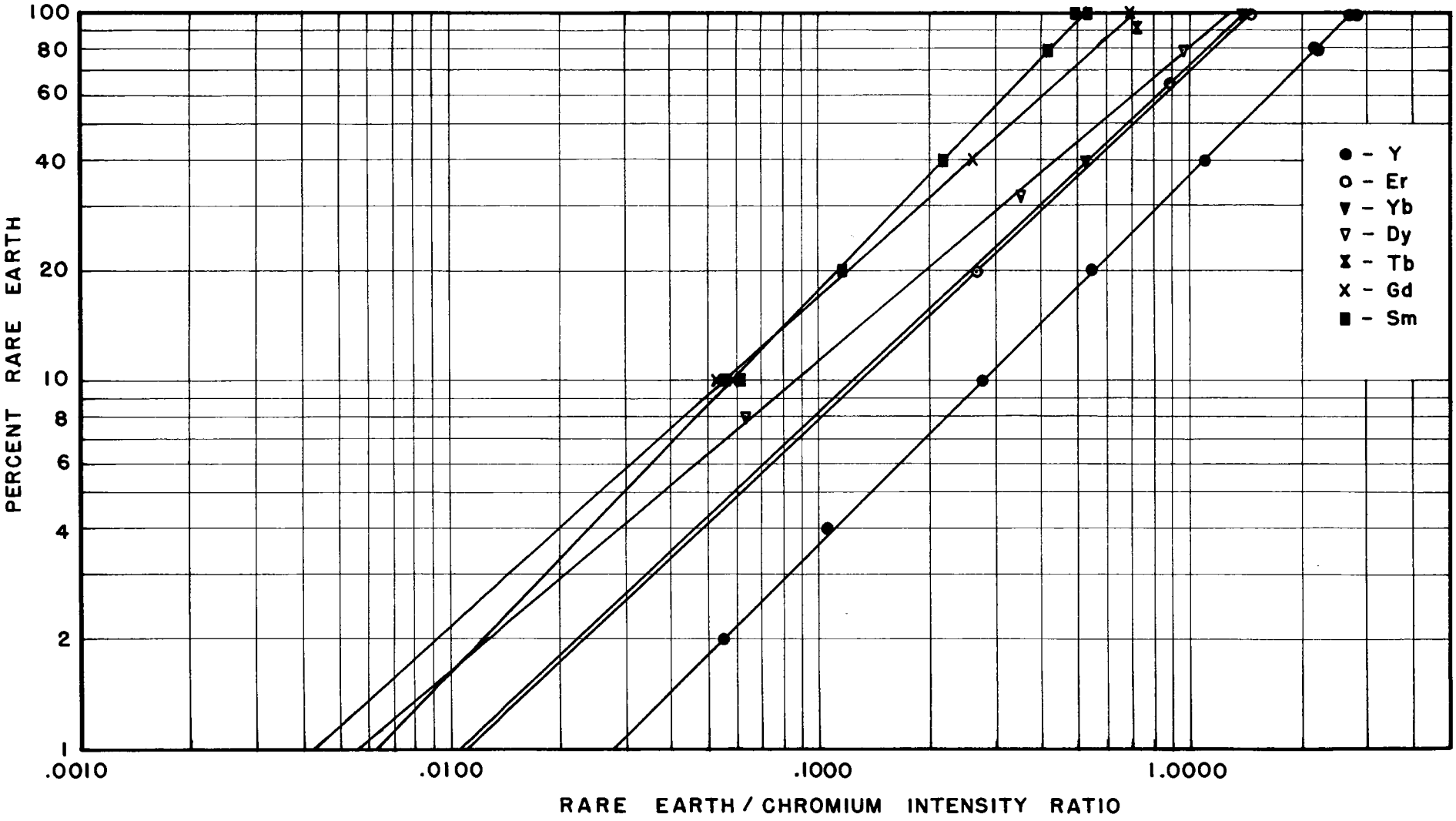

FIGURE 3. PERCENT RARE EARTH VERSUS RARE EARTH / CHROMIUM INTENSITY RATIO FOR DILUTED RARE EARTH SAMPLES

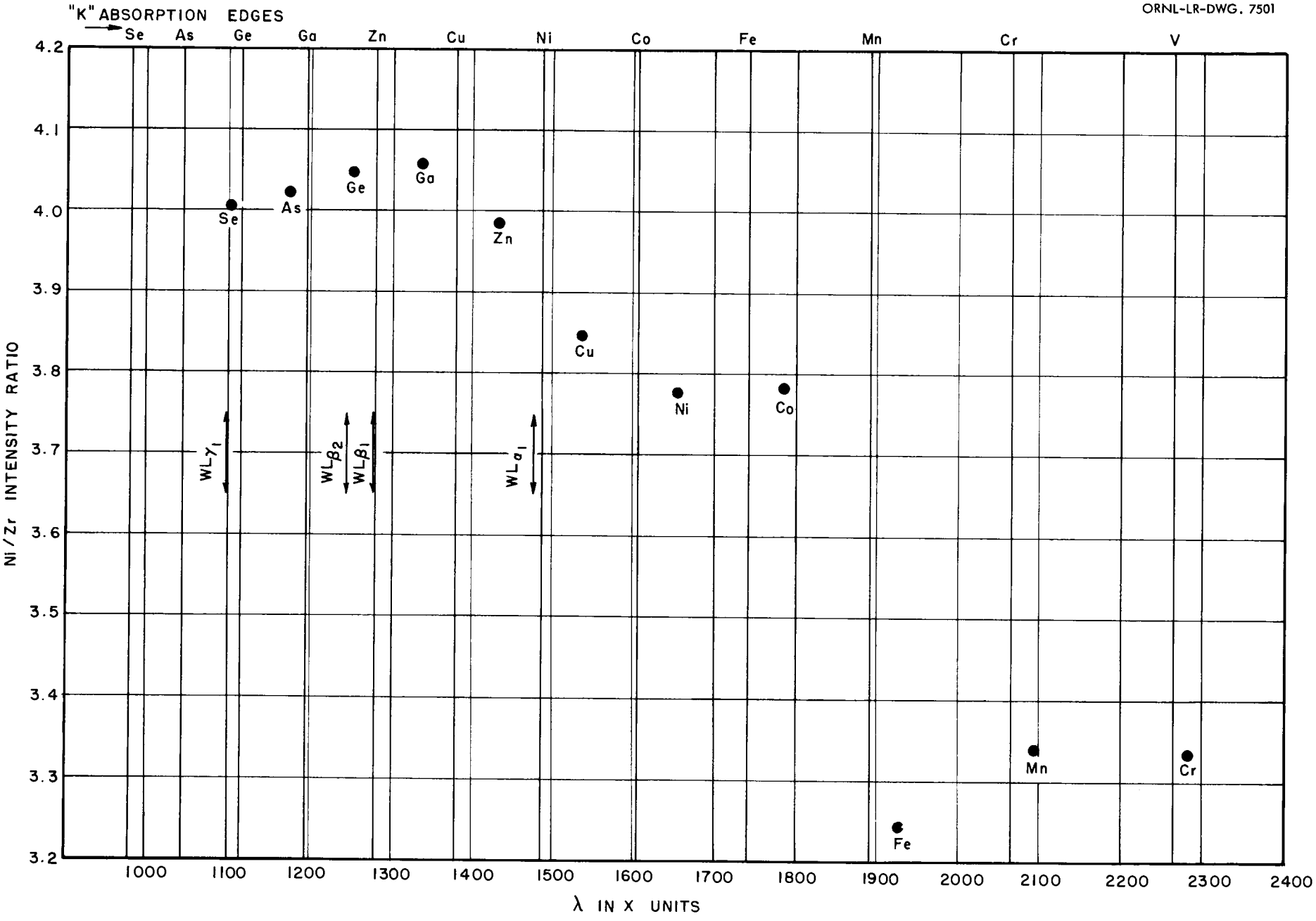

FIGURE 4. Ni/Zr INTENSITY RATIO VERSUS WAVELENGTH OF IMPURITY

less, leaving more to excite the chromium thereby causing the slope of the lines to decrease.

EXPERIMENTAL INVESTIGATION OF INTERFERENCES

The fourth period elements were chosen to investigate experimentally the nature and magnitude of the interferences described above because large quantities of chemically pure samples of these materials were available and the wave length range of the fairly simple "K" spectra of these elements is approximately the same as the "L" spectra of the rare earth elements (see Table I and Table IV). Zirconium was chosen as the reference element because it gives a situation similar to that of chromium as an internal standard in the rare earth analysis. Nickel was chosen as the "unknown" element because it is near the center of the group and therefore should be sensitive to the effects described above.

A series of buttons containing 0.225 gram of nickel oxide and 0.225 gram of zirconium oxide with 0.050 gram of impurity and 1.000 gram of corn starch were prepared. The reference button contained 0.250 gram of nickel oxide, 0.250 gram zirconium oxide and 1.000 gram corn starch to keep the total mass constant. The individual impurities selected were oxides of chromium, manganese, iron, cobalt, copper, zinc, gallium, germanium, arsenic or selenium. Data on these buttons were obtained in the manner described above for the rare earth elements.

Figure 4 shows the observed Ni/Zr intensity ratio versus the $K\alpha_1$ wave length of the interfering impurity. The "K" absorption edges of these impurities and the W "L" emission lines are also included (a W target X-ray tube was used). From this graph these effects may be seen:

A. Excitation effects due to $K\alpha$ and $K\beta$ lines of the contaminants.

TABLE IV

WAVE LENGTH IN X UNITS OF THE X-RAY EMISSION LINES AND ABSORPTION EDGES*

Element	$K_{\alpha 1}$ Line	$K_{\alpha 2}$ Line	$K_{\beta 1}$ Line	"K" Absorption Edge
Cr	2285.00	2288.89	2080.60	2065.95
Mn	2097.51	2101.44	1906.30	1892.54
Fe	1932.07	1936.00	1752.99	1739.83
Co	1785.31	1789.17	1617.48	1604.87
Ni	1654.50	1658.34	1497.08	1485.02
Cu	1537.40	1541.22	1389.36	1377.65
Zn	1432.22	1436.04	1292.61	1280.70
Ga	1337.33	1341.23	1205.41	1193.26
Ge	1251.48	1255.43	1126.62	1114.27
As	1173.44	1177.43	1055.13	1042.86
Se	1102.48	1106.52	990.12	977.08
Zr	784.30	788.51	700.28	687.38

Element	$L_{\alpha 1}$ Line	$L_{\beta 1}$ Line	$L_{\beta 2}$ Line	$L_{\gamma 1}$ Line
W	1473.37	1279.18	1242.07	1096.31

* Wave lengths were obtained from Cauchois and Hulubei[6].

With selenium, arsenic, germanium, and gallium as a contaminant, the Ni/Zr intensity ratio is high compared to the pure Ni/Zr intensity ratio. The Ni/Zr intensity ratio increases from selenium to gallium because both the K_α and K_β emission lines of these elements are on the short wavelength side of the Ni "K" absorption edge and the efficiency of Ni excitation by these impurities increases as the wavelength of the exciting fluorescence lines approach the "K" absorption edge of the nickel.

B. Conflicting excitation and absorption effects

With zinc as a contaminant, the Ni/Zr intensity ratio is high but not as high as with gallium as a contaminant though zinc is nearer the "K" absorption edge of nickel and will excite the nickel "K's" more efficiently than the gallium. In this case, the tungsten L_{β_1} line from the X-ray tube target is on the short wavelength side of the zinc "K" absorption edge thereby exciting the zinc "K" lines (see Figure 5) and in so doing being absorbed very efficiently by the zinc leaving less radiation from the X-ray target to excite the nickel "K" spectrum but giving more fluorescence radiation from the zinc to excite the nickel "K" spectrum. The net result of these conflicting effects appears to be a slight decrease in the radiation available to excite the nickel "K" spectrum causing the Ni/Zr intensity ratio to be slightly lower than with gallium as the contaminant but still higher than with no contaminant present.

C. Excitation effect of only the K_β line of the contaminant

With copper as a contaminant, the Ni/Zr intensity ratio is lower than

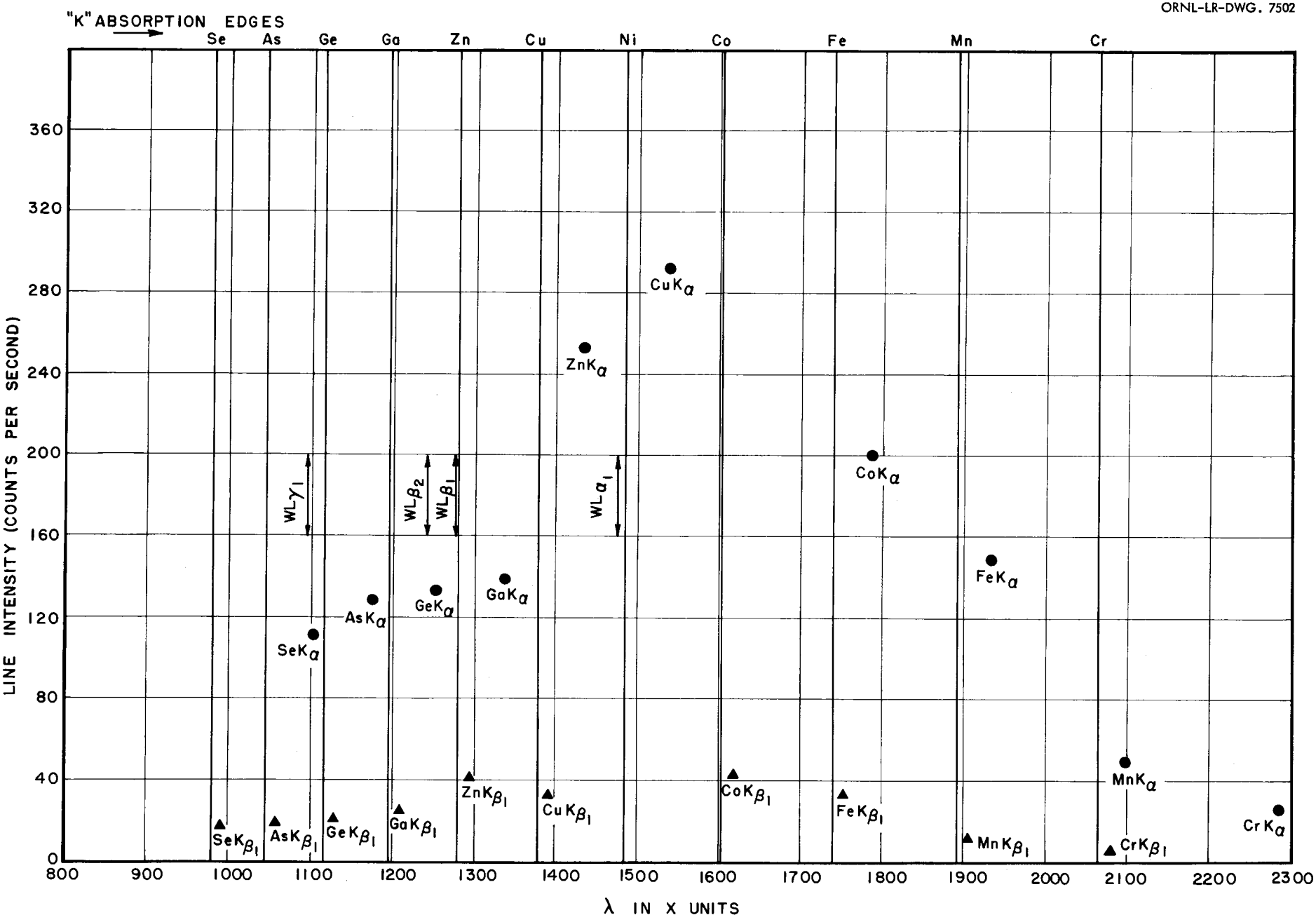

FIGURE 5. INTENSITY OF K_α AND K_{β_1} IMPURITY LINES VERSUS WAVELENGTH

those previously discussed but still a little higher than the one which contained no contaminant. Since the copper $K\beta$ line is of shorter wave length than the nickel "K" absorption edge, it will excite the nickel "K" spectrum; however, the more intense copper $K\alpha$ lines are of longer wave length than the nickel "K" absorption edge and will not excite the nickel "K" spectrum.

D. No characteristic excitation or absorption effects present

With Co as a contaminant, the Ni/Zr intensity ratio is about normal. The Co "K" spectrum is on the long wave length side of the "K" absorption edge of nickel and therefore will not selectively excite the nickel "K" spectrum. The nickel $K\alpha$ lines are on the long wave length side of the cobalt "K" absorption edge, and thus are not absorbed to a very great extent by the Co.

E. Absorption effects of the contaminant

With the elements from iron to chromium, the Ni/Zr intensity ratio is considerably lower than with no contaminant present. The nickel $K\alpha$ lines are on the short wave length side of the "K" absorption edges of these impurity elements and for this reason are strongly absorbed. Since the wave length of the nickel $K\alpha$ lines is just short of the "K" absorption edge of iron, the nickel line intensity is reduced more by iron than by the manganese and chromium impurity.

The wave length of the "K" absorption edge and "K" spectrum of zirconium is far enough from the wave length region of these elements to give little cross

interference between absorption edges and lines. However, a small absorption effect was noted that was uniform throughout the series (see Figure 6). As the atomic number of the contaminant increased, the intensity of the zirconium Kα radiation decreased. Since this change was small and uniform the effects discussed previously can be ascribed to the nickel and not the zirconium.

The maximum impurity effects on the Ni/Zr intensity ratio were observed in the cases of gallium and iron. The presence of ten per cent gallium changed the Ni/Zr intensity ratio from 3.78 to 4.06 or + eight per cent; whereas, ten per cent iron changed the Ni/Zr intensity ratio from 3.78 to 3.25 or -14 per cent. Thus, it can be concluded that the presence of ten per cent of another element may bias the determination of two or more elements by the same order of magnitude. Hence, significant corrections for complex mixtures will be necessary.

APPLICATIONS AND LIMITATIONS

X-ray fluorescence analysis would be best for binary and possibly ternary mixtures, but could be used successfully on even complex mixtures for specification type of analysis where only small changes in composition would take place. Once the exact intensity ratios for each element and reference were established for the normal concentration, a slight variation in one or two elements could be detected and, if working curves were established, could be evaluated quite accurately.

For other than specification type analysis, it would be difficult to obtain an accurate quantitative analysis of a group of several consecutive elements because of the many cross interferences which will be present, even using the simplest spectrum possible, the "K" spectrum. However, it may be possible in some cases, with plenty of pure standards available and with properly chosen internal standards, to correct to some extent for these cross interferences and obtain

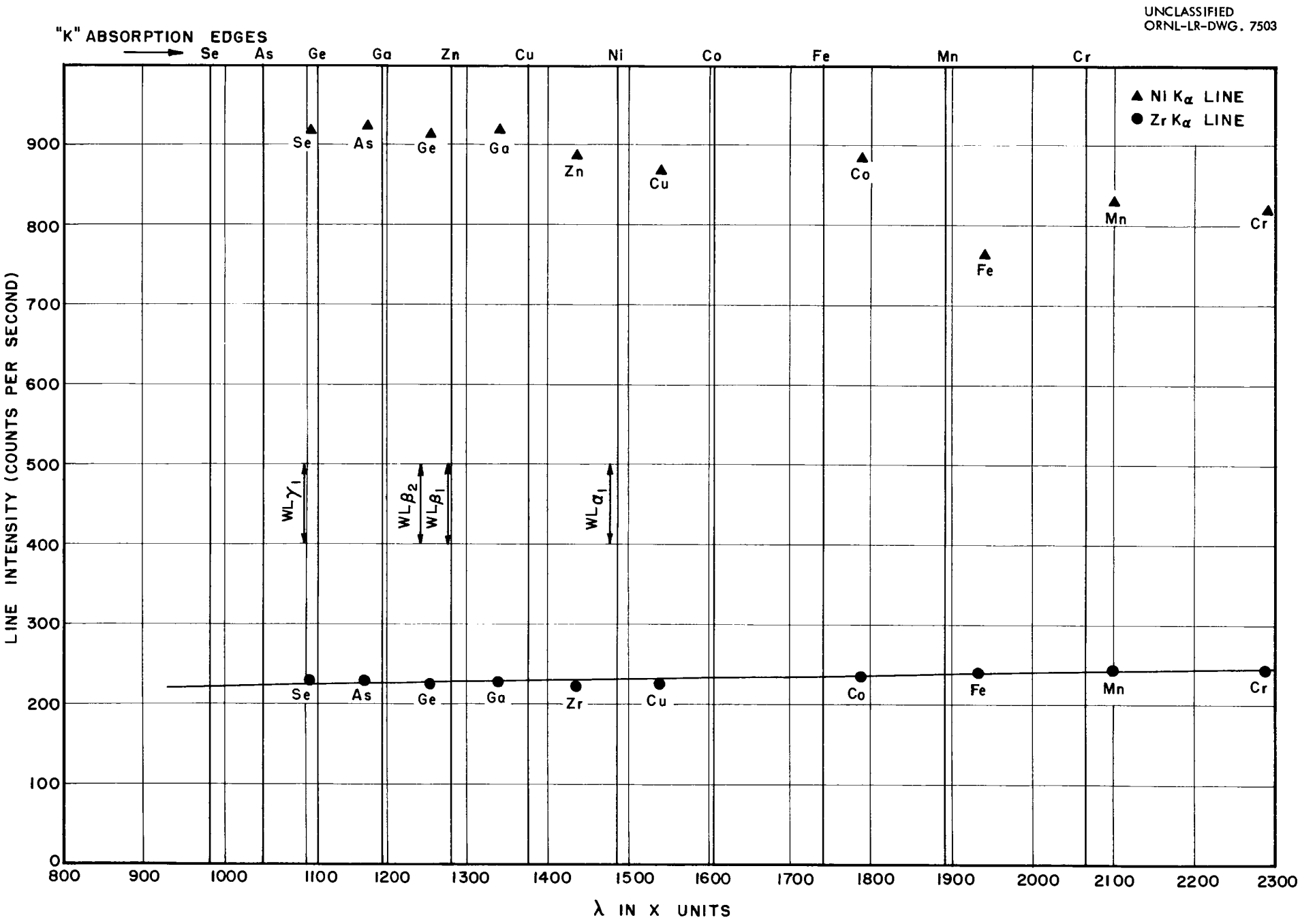

FIGURE 6. INTENSITY OF Ni K_α AND Zr K_α LINES VERSUS WAVELENGTH OF INTERFERING IMPURITY

fairly accurate analyses.

Another limitation of the X-ray fluorescence method of analysis is the relatively poor lower limit of detection. With our present equipment with its fairly low X-ray intensity, it is difficult and time consuming to obtain directly an analysis for concentrations less than one per cent. The new high intensity equipment now available from X-ray manufacturers should make possible fairly accurate analysis of lower concentrations of some elements in a reasonable length of time if only two or three elements were present or if specification type of analysis were being used. (If very high counting rates are obtained, resolving time corrections must be made and the high voltage source for the X-ray tube suitably filtered to take out the ripple. To date, we have found no accurate method of correcting for resolving time losses without a constant potential on the X-ray tube[2].)

In general, for the low concentrations, the emission spectographic method of analysis would be better while for high concentrations the X-ray fluorescence method of analysis would be better (see Table V). However, under some conditions, the X-ray fluorescence method of analysis may have some advantages over the emission spectographic method of analysis for fairly low concentrations because some solid samples, coatings or films on solid samples, powder samples and liquid samples can be analyzed without destroying, damaging or contaminating the sample. This could be quite an advantage where very rare, costly samples or samples difficult to reproduce or replace were involved.

TABLE V

ACCURACY OF RARE EARTH ANALYSIS BY X-RAY FLUORESCENCE*

< 10 per cent range	± 60 per cent
10 - 20 per cent range	± 13 per cent
20 - 50 per cent range	± 9 per cent
> 50 per cent range	± 3 per cent

All percentages are based on the 95 per cent limit of error.

* The emission spectographic method claims an accuracy of ± 10 per cent.

CONCLUSIONS

It is difficult to obtain a direct analysis of rare earths or other complex groups of elements by the X-ray fluorescence method. In general, fairly good accuracy can be obtained for high concentrations; though, in some cases, corrections for impurities must be made. For determination of concentrations below ten per cent, very important corrections must be made unless specification type analysis is being used, i.e., when closely matched standards are available. By determining the effect of each element on all the others, it may be possible under certain conditions to obtain a fairly accurate determination of concentrations as low as one per cent on some complex mixtures.

ACKNOWLEDGMENTS

The author would like to express his appreciation to W. F. Peed and J. R. McNally, Jr., of this laboratory for their invaluable assistance on this project. Also, he would like to express his appreciation to the Isotope Chemistry group for the pure samples of the rare earth oxides, to J. J. Mundzak for the rare earth oxide samples which he had analyzed by the emission spectographic method, and to the Ceramics Laboratory for the use of their press.

BIBLIOGRAPHY

1. Application of X-Ray Fluorescence to Analysis of Zirconium in Uranium, W. F. Peed, W. B. Wright, Jr., and G. L. Rogosa, Oak Ridge National Laboratory Report No. ORNL-1419, January 23, 1953.

2. Preliminary Investigation of Monochromatic X-Ray Absorption as a Method of Analysis for Uranium, W. F. Peed and H. W. Dunn, Oak Ridge National Laboratory Report No. ORNL-1265, April 8, 1952.

3. Analysis of Rare Earths by Secondary X-Ray Emission Spectra Using a High Intensity X-Ray Source and a Geiger Counter Spectometer, G. L. Clark, W. F. Wagner and D. W. Carley, University of Illinois, N6 ori 71 - Chemistry Task No. VII, August 18, 1947.

4. Analysis of Rare Earth Mixtures by Fluorescence X-Ray Spectrography, Merlyn L. Salmon and James P. Blacklodge, American Chemical Society meeting, Omaha, Nebraska, November 4 to 6, 1954.

5. A Geiger Counter Spectrometer for X-Ray Fluorescence Analysis, H. Friedman and L. S. Birks, Rev. Sci. Inst. 19, 323 (1948).

6. Calibration Method for X-Ray Fluorescence Spectroscopy, H. J. Beattie and R. M. Brissey, Anal. Chem. 26, 980 (1954).

7. Longueurs D'Onde Des Emissions X ET Des Discontiniuties D'Absorption X, Y. Cauchois et H. Hulubei, (Hermann et Cie, Editeurs, 6, Rue de la Sorbonne, 6, Paris, 1947).

8. X-Rays in Theory and Experiment, A. H. Compton and S. K. Allison, (D. Van Nostrand Company, Inc., New York, 1935).

9. Quantitative Spectrochemical Analysis of Rare Earth Mixtures, J. A. Norris and C. E. Pepper, Anal. Chem. 24, 1399-1403 (1952).

10. Chemical Analysis by X-Rays and Its Applications, Georg von Hevesy, (McGraw-Hill Book Company, Inc., New York, 1932).