Mines Branch Investigation Report IR 73-57

THE DETERMINATION OF RARE EARTHS IN STEELS

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ABSTRACT

Synthetic standards were prepared for an investigation of the deter-mination of rare earths in steels because no suitable standards were available. Using these standards, it has been possible to establish a number of the samples submitted for analysis as secondary standards.

Using the first order K lines of cerium and lanthanum, these elements have been determined in steels in the range 0.002 - 0.16% with an error of 20 ppm or less when the X-ray tube was operated at 90 kV and 20 mA. When second order lines were used, the error was doubled.

It was found that the synthetic standards, which were in powder form, required a different method for the calculation of net counts than had been used in previous steel analyses. The method of preparing the standards has a significant effect on the background counts.

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INTRODUCTION

Requests were received for the determination of cerium and of cerium and lanthanum in experimental and line pipe steels. The rare earths were added to the steels as mischmetal, lanceramp and rare earth silicides. The expected concentration was 0.1% maximum for cerium and correspondingly less for lanthanum.

No standards were available, so it was necessary to make synthetic ones as was done for the estimation of zirconium (1), niobium (2) and hafnium (3) in steels.

No attempt has been made to determine the other rare earths present. They occur in the additives in much smaller quantities than do cerium and lanthanum; therefore, their estimation would be difficult with our present equipment.

SYNTHETIC STANDARDS

Synthetic standards are prepared from electrolytic iron with additions of the element in question. The components are dissolved and the solution is taken to dryness. The residue is baked to ensure the removal of all moisture, then is ground to -200 mesh in an agate mortar. Portions of the samples must be dissolved, dried, baked and ground for comparison with these standards. The percentage of the desired component, the mean of several analyses, determined for the powdered samples, is transferred to the corresponding solid samples. These then become secondary standards after several tests for correspondence between drillings and the bulk samples and for homogeneity.

The first set of standards had additions of lanceramp to correspond to the first samples received. When other standards having smaller additions

were required, CeO_2 and La_2O_3 were used to make it possible to vary the cerium: lanthanum ratio. In addition, a few standards were prepared with only one element added.

EXPERIMENTAL CONDITIONS

The K lines of the rare earths were used for their determination because the tungsten and molybdenum X-ray tubes equipping our spectrograph are not efficient exciters of their L lines. First order lines were used to establish the secondary standards, then second order lines were tested for sensitivity, using these standards where the level of addition permitted -- second order radiation has only one-quarter of the intensity of first order.

Figure 1 shows the 2θ position of K absorption edges and first order lines of cerium and lanthanum. Only $CeK\beta$ is affected by the lanthanum edge and none of the lines by the cerium edge. In addition to the K edges of the two rare earths, the K edge of iodine is significant. The iodine is found in the sodium iodide crystal of the scintillation counter and its presence reduces the intensity of the rare earth lines. They all suffer absorption by the iodine, as Figure 1 shows; the effect of the iodine is shown in Figure 4 by the decrease in the continuum at approximately 11^0 2θ.

As illustrated by the double plateau of $CeK\alpha$ shown in Figure 2, the elements may be determined by using a counter voltage lying between either 700 and 775 or 900 and 1000 volts. It was decided to use the lower voltage range to avoid the detection of any low energy radiation that might overshoot the crystal at low angles and enter the detector. A scan of a mild steel using a counter voltage of 750 is shown in Figure 3, where the second order is recorded at twice the sensitivity of the first order radiation. For this sample, which contained a relatively high level of rare earths, the first

order lines of cerium and lanthanum could not be separated by LiF(200), the crystal generally used for dispersion because of its high reflectivity; nor could they be separated by LiF(200), which has a narrower d spacing.

The full scan of one low alloy steel over the range of interest and the partial scan of another are shown in Figure 4 to illustrate the interference by lines of alloying elements with the second order lines of the two rare earths. Pulse amplitude distributions for MoKβ, the interfering line with the greatest energy, and for LaKα, the least energetic of the radiations to be counted, are given in Figure 5. By using the baseline of 10.5 V shown by the broken line in the figure, 95% of the molybdenum is eliminated, but this does not suffice for samples containing significant amounts of this element as the 10.5 V scan in Figure 4 illustrates. A 12 V baseline had to be used for samples counted at the second order, although it removes 25% of the lanthanum radiation, as the dotted line in Figure 5 makes evident.

A comparison of Figures 3 and 4 in the low 2θ region illustrates the range in intensity of the first order lines experienced in this investigation. The obvious peaks in Figure 3 are almost indistinguishable in Figure 4, while the iodine absorption edge at 10.65°, masked by the Kα lines in Figure 3, is apparent in Figure 4. For the lines of low intensity, the standard deviation of the background counts can be as large as the net peak counts of the elements and, depending on whether the deviation of a particular count is positive or negative, it can effectively wipe out or double the peak counts at these levels.

The X-ray tube was operated at 90 kV and 20 mA throughout the investigation and the counter at 725 V. The baseline setting was 6 V for first order counts and 12 V for second order.

ANALYSIS WITH SYNTHETIC STANDARDS

Determination of Net Counts

Backgrounds for the first order lines were counted at 11.6^0 and 13.0^0 2θ. They were well removed from the peaks of the elements and separated from them by the iodine absorption edge and the crown of the continuum maximum.

In previous X-ray analyses, when lines have occurred on the slope of the continuum or near its maximum, net counts have been obtained by using a blank ratio method. For this, replicate measurements are made on a number of blanks and the ratios of the peak to the background counts for these are determined. The mean ratio is then used to determine the background under the peak from the counted background for each sample and this calculated background is subtracted from the peaks counts of the sample to give the net counts.

In the case of the synthetic standards, the following ratios were obtained:

from quadruplicate counts on four blanks:	Ce/11.6^0	0.9196 ± 0.0066
	Ce/13.0^0	1.0450 ± 0.0101
	La/11.6^0	0.9682 ± 0.0074
	La/13.0^0	1.0977 ± 0.0103
from standards containing La but no Ce:	Ce/11.6^0	0.9272 ± 0.0052
	Ce/13.0^0	1.0572 ± 0.0056
from standards containing Ce but no La:	La/11.6^0	0.9774 ± 0.0062
	La/13.0^0	1.1173 ± 0.0099

The backgrounds for both elements were raised when the other was present indicating an unexpected mutual enhancement. The differences were within the two sigma limits of the blanks, but were significant in that they all increased.

In Figure 6 the net counts obtained for the standards using the 11.6^0 background are plotted against the concentration of the element present.

The values used are the means of duplicate counts on the standards taken on two days. For lanthanum, all the points fall along the same line, indicating no enhancement; but, for cerium, there are fewer counts for the standards that contain only that element, showing an apparent increase in counts for cerium in standards that contain lanthanum as well.

A line calculated from the individual counts for the standards with cerium only had the equation: $Y = 0.000111X - 0.00157$, where Y is the %Ce and X the net cps. This line was used to determine the counts due to cerium, in the other standards and the excess CeKα cps were plotted against the LaKα net cps. Using results only from standards, where the net counts for both elements exceeded 50 cps, to accommodate counting errors, a line was calculated to determine the cerium counts due to lanthanum. This correction was applied to the cerium counts from standards containing both elements, again using the 50 cps exclusion, and a further line was calculated for these corrected counts. It had the equation: $Y = 0.000110X - 0.000187$. This is in excellent agreement with the line above and indicates that the correction seems acceptable.

Although this correction method seemed acceptable, it was not logical that the correction was not a mutual one. Moreover, though it was possible to determine a correction for the synthetic standards, it wouldnot be possible to calculate one to be applied to the secondary standards and bulk samples because no steels having single known rare earth additions were available.

The net cps and peak to background ratios had been calculated on a desk computer and only the desired information had been printed out. It was decided to go back and scrutinize all counts thoroughly. After the counts had been tabulated, it was noticed that the background counting rates were not consistent:

	n	11.6^0	13.0^0
for blanks	24	3871 ± 116	3533 ± 104
for standards with lanceramp	10	3769 ± 55	3448 ± 47
for standards with CeO_2 and/or La_2O_3	34	4309 ± 564	3799 ± 762
for sample powders	22	4008 ± 238	3642 ± 201

n is the number of replicates upon which the mean values are based, not the number of synthetic standards or steel powders. It is readily seen that the much higher backgrounds of the second group of standards would affect the net cps significantly; this probably accounts for the differences in cerium response in Figure 6.

To try to compensate for this variation in background, it was decided to use 13.0^0 as the reference background, because it is farthest removed from the peaks and the iodine absorption edge, and to correct all other counts by ratios to it. Thus three mean ratios were calculated from counts on the blanks: $Ce/13.0^0$, $La/13.0^0$ and $11.6^0/13.0^0$. The CeKα corrected net cps were calculated as $(Ce_S - 13.0^0_S \times Ce/13.0^0) - (11.6^0_S - 13.0^0_S \times 11.6^0/13.0^0)$ using the mean ratios from the blanks and the individual cps from the samples. Peak and 11.6^0 net cps were calculated by reference to the 13.0^0 counts for each sample and the difference between the two was taken as the corrected net counting rate for the cerium present. Using these corrected net cps, all the points for CeKα from the synthetic standards, which had formerly given two lines, now fell along one line and counts from the powdered samples could be compared with them. The mean ratios determined from four replicate counts on six blanks were: $11.6^0/13.0^0$ 1.0956 ± 0.0030

$\qquad$ CeKα/13.0^0 0.9962 ± 0.0049

$\qquad$ LaKα/13.0^0 1.0400 ± 0.0066

Discussion

In an interim report (3) on the determination of rare earths in steels   difference in the response of the cerium in synthetic standards was related to the amount of lanthanum present and was corrected for it as outlined above. After examination of the background counts, the significant difference between the two groups of standards made this premise, unsatisfactory from a theoretical viewpoint, even more untenable.

In the preparation of synthetic standards, the electrolytic iron was dissolved in hydrochloric acid. The lanceramp added to the first group of standards had been dissolved in this acid also. The CeO_2 added to the second group had been dissolved with difficulty in hot sulphuric acid and the La_2O_3 readily in dilute nitric acid. The mixed solutions had been taken to dryness and baked to remove the acid residues, but the presence of the different acids in the standards had probably affected the nature of the iron compound that separated from solution and this difference may have been responsible for the variation in background counts. The difference in counts between the two groups of standards was due to matrix difference; it was not an interelement effect, although, in this instance, the two effects were parallel. The amount of nitric acid present was directly proportional to the amount of lanthanum, which had been added by aliquots of a solution. Therefore, the correction attributed to the lanthanum could more correctly be ascribed to the nitric acid, but it was proportional to the lanthanum as well and could be readily related to it as shown previously. There is no ready means of correcting for the nitric acid content.

It is probable that the high standard deviation for the background counts of the second group of standards is due, in part, to the varying amounts of

sulphuric and nitric acids in the solution from which they precipitated. Such variation had not been observed in the synthetic standards used for the determination of other elements in steels because the acid base in the other cases had been consistent. In any future work involving the use of synthetic standards the effect of acid radicals must be borne in mind.

Determination of Cerium and Lanthanum

Using corrected net cps for both $CeK\alpha$ and $LaK\alpha$, the following lines were established from the synthetic standards:

for cerium : $Y = 0.8489X + 25.05$ $r = +0.9946$ $s_e = \pm27.36$

for lanthanum: $Y = 0.9066X + 6.70$ $r = +0.9931$ $s_e = \pm19.82$

Where Y and s_e, the standard error of prediction, are in ppm, and X is the corrected net counting rate. The correlation coefficient, r, is a measure of the scatter of the points about the line, perfect correlation being unity.

Second order lines were also set up and found to have the following equations:

for cerium : $Y = 5.7578X + 24.08$ $r = +0.9521$ $s_e = \pm45.08$

for lanthanum: $Y = 4.7370X + 13.55$ $r = +0.9932$ $s_e = \pm15.36$

The intensity of second order lines is approximately one-quarter of that of first order lines. This loss, plus that caused by discrimination against interference at the second order, is measured by the difference in the slopes of the lines: for the first order, 1 cps $CeK\alpha$ is equivalent to less than 1 ppm of cerium; for the second order, to more than 5 ppm. As the counting rate decreases, the counting error increases unless long counting times are used. This increase is partly responsible for the poor correlation found for the cerium line, where the errors have been compounded because it was necessary to again correct cerium for matrix variation using the lanthanum counts for the purpose.

Lines were also calculated, using peak to background ratios for both orders, with suitable corrections applied to the cerium counts. The correlation and error for these lines were of the same order as those shown above.

SECONDARY STANDARDS

Using the above lines, and those for the peak to background ratios as well, the powders prepared from drillings from the early samples submitted were analyzed for cerium and lanthanum. The means of the analytical results were transferred to the corresponding bulk samples which then became secondary standards.

Using the secondary standards, lines were established and samples could then be analyzed directly. As more samples were analyzed, appropriate ones were recounted on successive days to establish them as additional secondary standards to extend and to fill gaps in the original range.

With the secondary standards, there was, of course, no matrix effect to be compensated for, so simple net counts, calculated by background factors from blanks, were used, i.e., Ce net cps = $Ce_s - 11.6^0_s \times Ce/11.6^0$ or $Ce_s - 13.0^0_s \times Ce/13.0^0$. Both background corrections resulted in the same net cps within a few counts, as would be expected. The regression lines calculated from both sets of counting rates were:

for cerium: : $Y = 0.7997X + 0.7938$ $r = +0.9996$ $s_e = \pm12.67$

for lanthanum: $Y = 0.7894X + 7.9724$ $r = +0.9941$ $s_e = \pm16.74$

The slopes are of the same order as those for the lines for the synthetic standards and the correlation and error are slightly improved, as they should be with the packing error eliminated.

For the second order, counts were taken at three backgrounds and the net cps were calculated from each one by the blank ratio method. The combined

results gave the equations:

for cerium   : $Y = 3.9718X + 0.4504$ $r = +0.9966$ $s_e = \pm 45.34$

for lanthanum: $Y = 4.7424X - 25.2394$ $r = +0.9983$ $s_e = \pm 17.08$

The mean background counts obtained on the blanks were: at 23.0^0 624 cps, at 24.0^0 582 cps and at 25.0^0 540 cps.   All had standard deviations of 6 cps.   These values plot as a straight line.   If extrapolated, this line does not give values at the peaks equivalent to the mean obtained for them from blanks.   For $CeK\alpha$ the actual mean was 754 rather than 734, obtained by extrapolation, whereas for $LaK\alpha$, the corresponding figures were 686 and 701 cps.   The continuum is curved in the region of the second order peaks and background extrapolation does not give reliable results, although such a procedure has proved valuable in other cases.   Blank ratios must be used.

The samples chosen for use as blanks and standards were counted a number of times to determine the mean value to be assigned to them, and were given a cursory homogeneity test by repeating the counts after each of three successive turns through an angle of 90^0 to ensure that comparable counting rates were obtained regardless of the orientation of the standard in the X-ray beam.   Several were discarded after this test.   As a matter of information, the four successive first order counts were used to determine net counts from both backgrounds and corrected net counts with respect to 13.0^0. Typical mean cps obtained by these calculations for a range of values were as follows:

| Sample | CeKα net | | | LaKα net | | |
	11.6^0	13.0^0	corrected	11.6^0	13.0^0	corrected
7819	2044	2061	2041	1118	1135	1126
7890	1028	1037	1026	524	533	524
7909	852	845	851	456	449	456
8326	412	418	410	274	279	274
3595	47	58	55	32	42	32

From these results, it is evident that any background correction may be used providing sufficient replicate counts are taken on a number of blanks to establish firm ratios.

DISCUSSION

The sensitivity of the X-ray spectrographic method for the determination of rare earths is satisfactory for the samples currently being received. With reasonable counting times, 20 ppm of cerium or lanthanum may be determined in these samples using first order radiation. If more than 0.2% is present, the lines of these elements will suffer mutual interference and second order lines will have to be used. Any attempt to determine neodymium or praseodymium, which are present in small amounts in some of the innoculants, will have to be postponed until greater sensitivity is achieved through improved instrumental components.

Most of the published methods for the determination of rare earths by X-ray spectrography are for ore samples. The methods may involve fusion, separation of the rare earths from solution by precipitation, or concentration by ion exchange. None of these approaches is attractive for the analysis of steel.

Cerium has been determined in nodular iron in the 0.01 to 0.1% range using its L lines and a chromium-target tube (5). When time permits, it is proposed to look at the L lines of the standards established in this investigation, with the equipment set up for the on-stream analysis of ores which includes a chromium tube. However, for these L lines, a vacuum path would increase the sensitivity and this is lacking.

CONCLUSIONS

Cerium and lanthanum may be determined in bulk steel samples in the 0.002 to 0.2% range by X-ray spectrography using the first order K radiations of these elements. For higher concentrations, second order lines should be used.

If synthetic standards are needed, care must be taken that acid residues do not affect the counts and that any matrix effect, caused by the use of more than one acid, is compensated by using a reference blank or other means.

ACKNOWLEDGEMENTS

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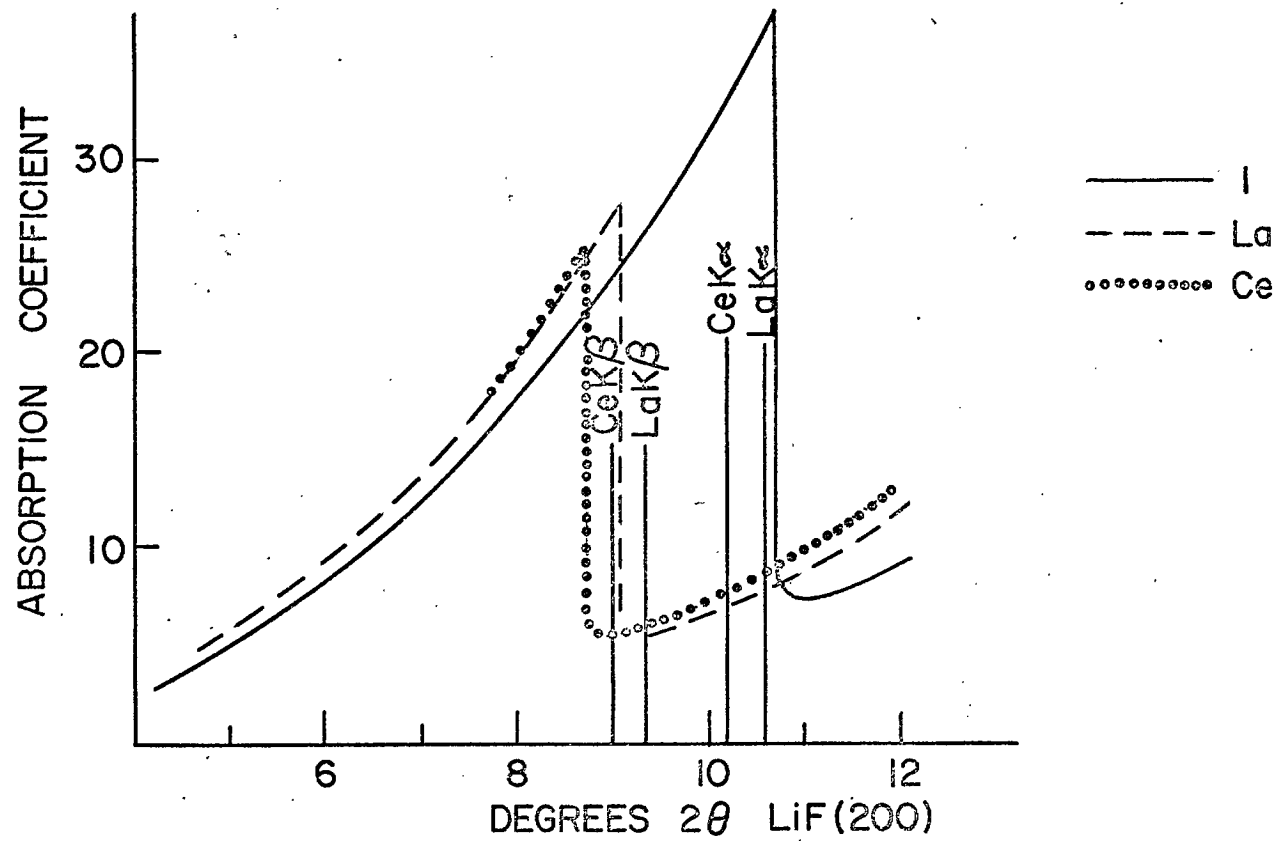
Figure 1: Absorption Edges and K Lines of Interest.
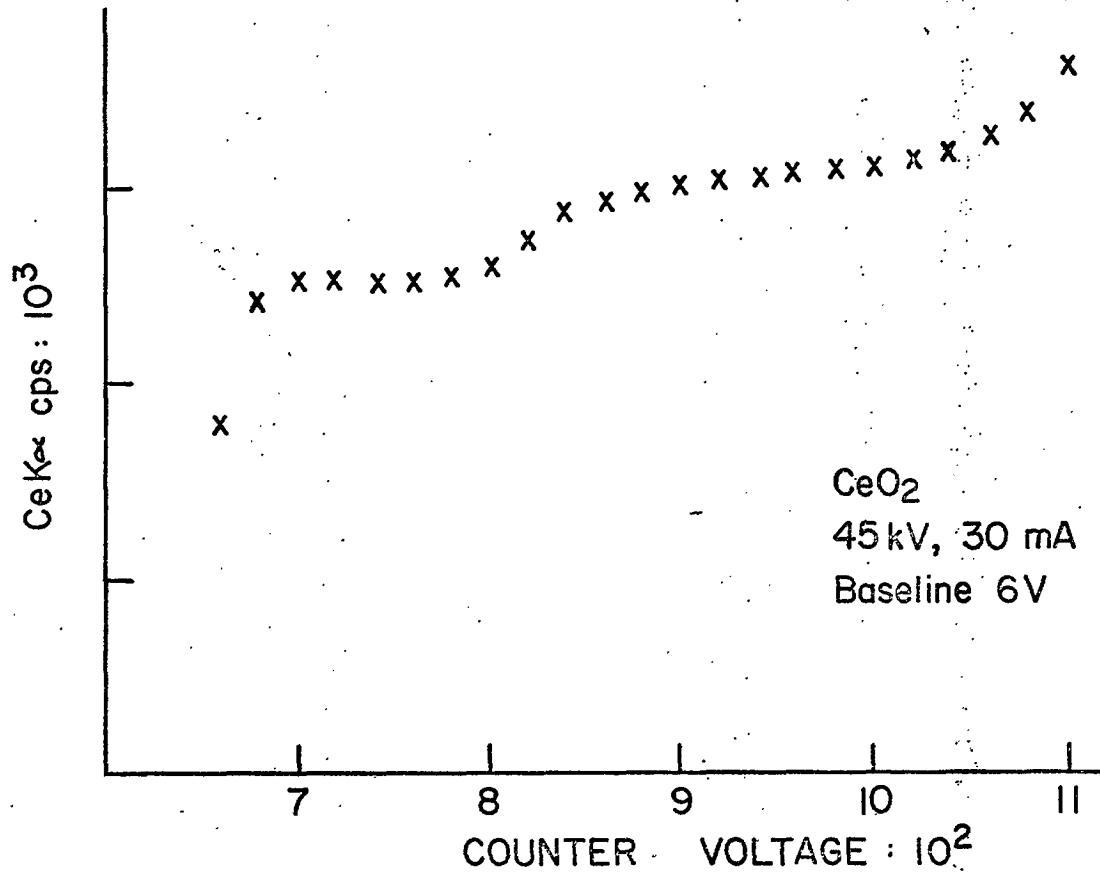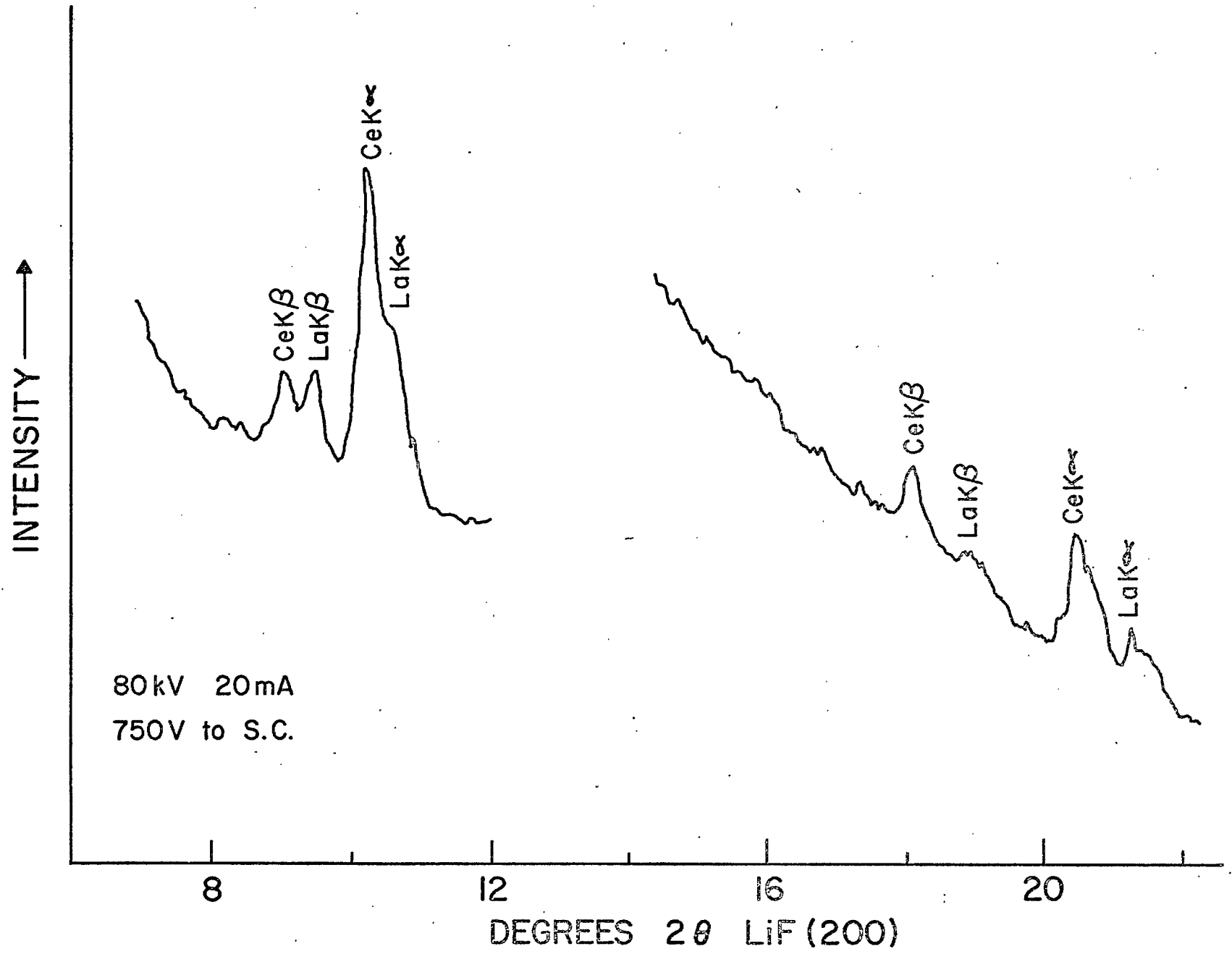
Figure 2: CeKα Response to Counter Voltage.

Figure 3: Scan of Mild Steel Sample.

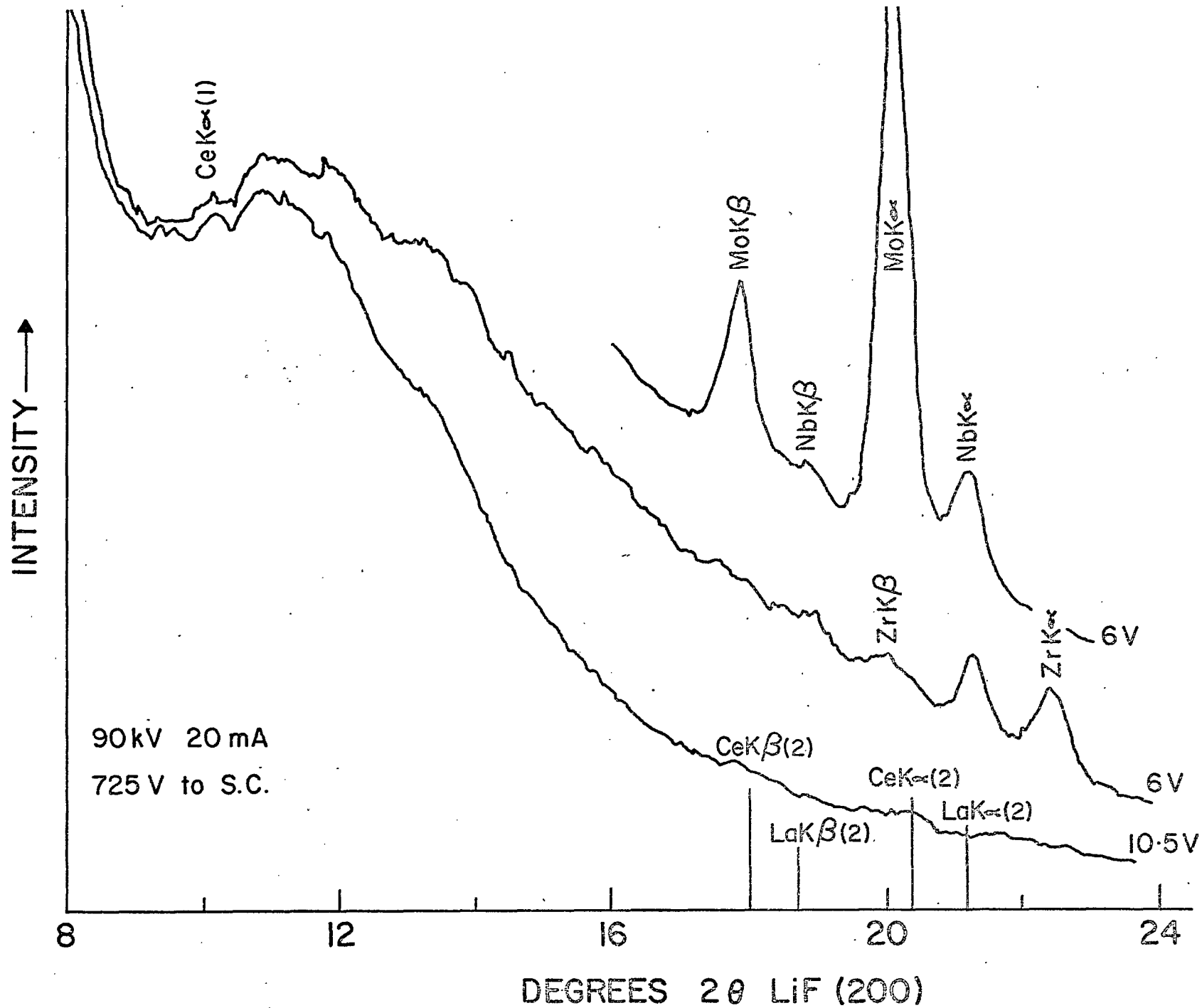Figure 4: Scans of Low Alloy Steels.
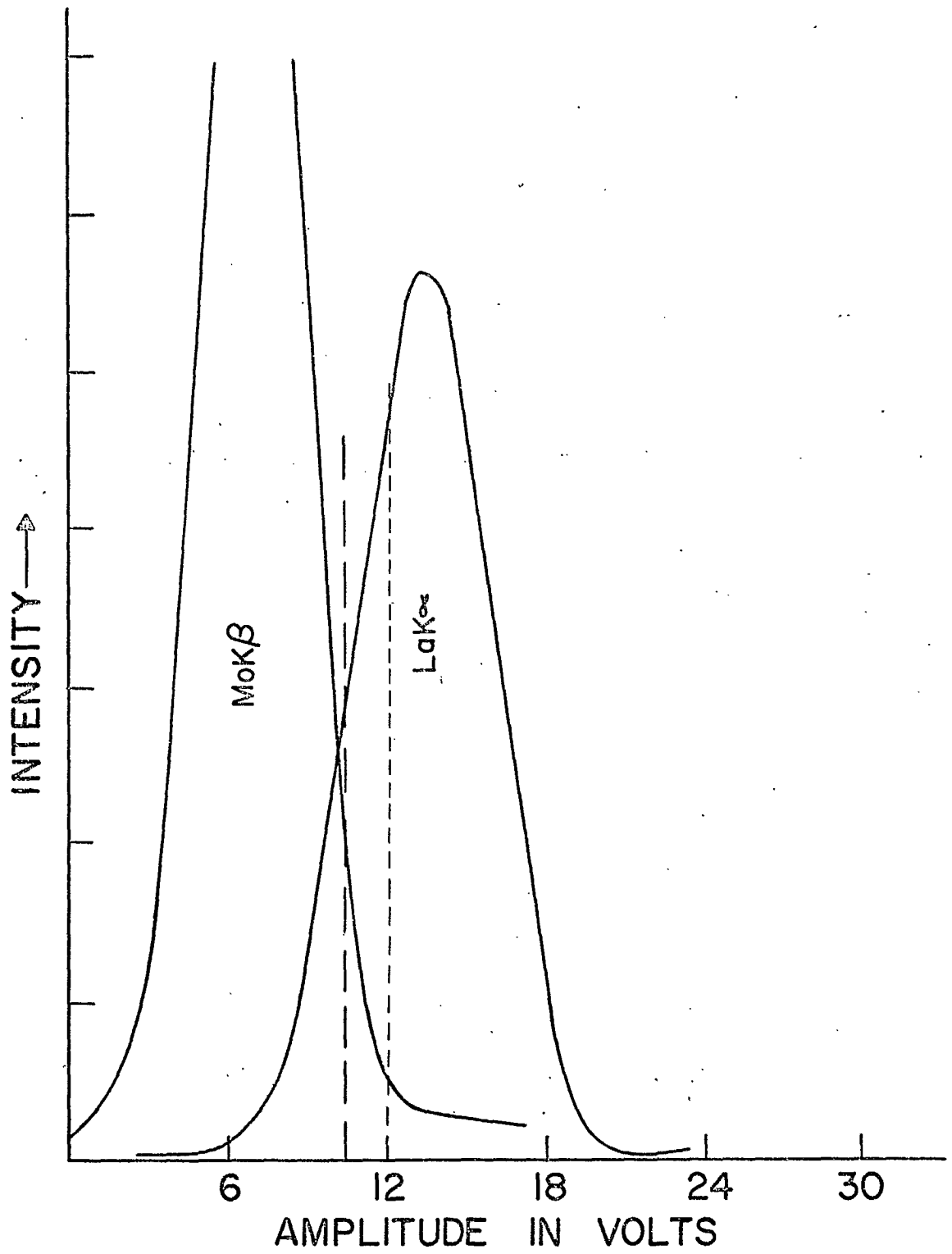
Figure 5: Pulse Amplitude Distribution for MoKβ
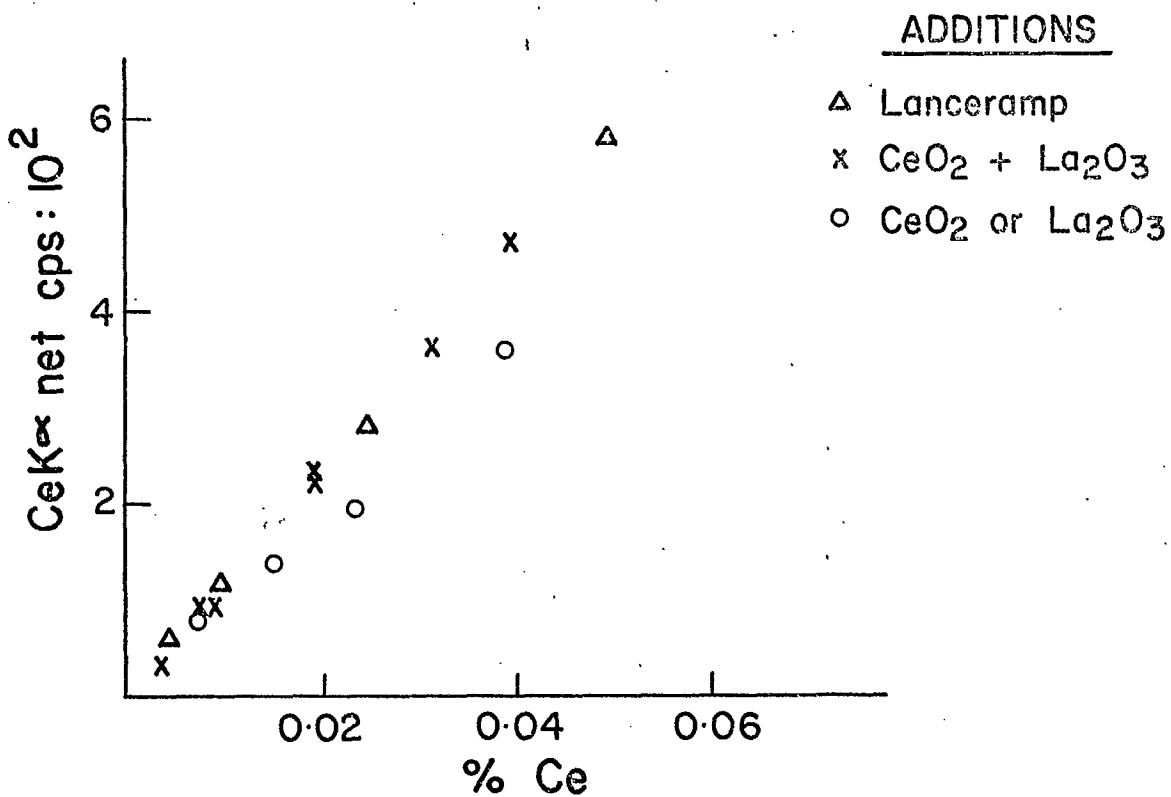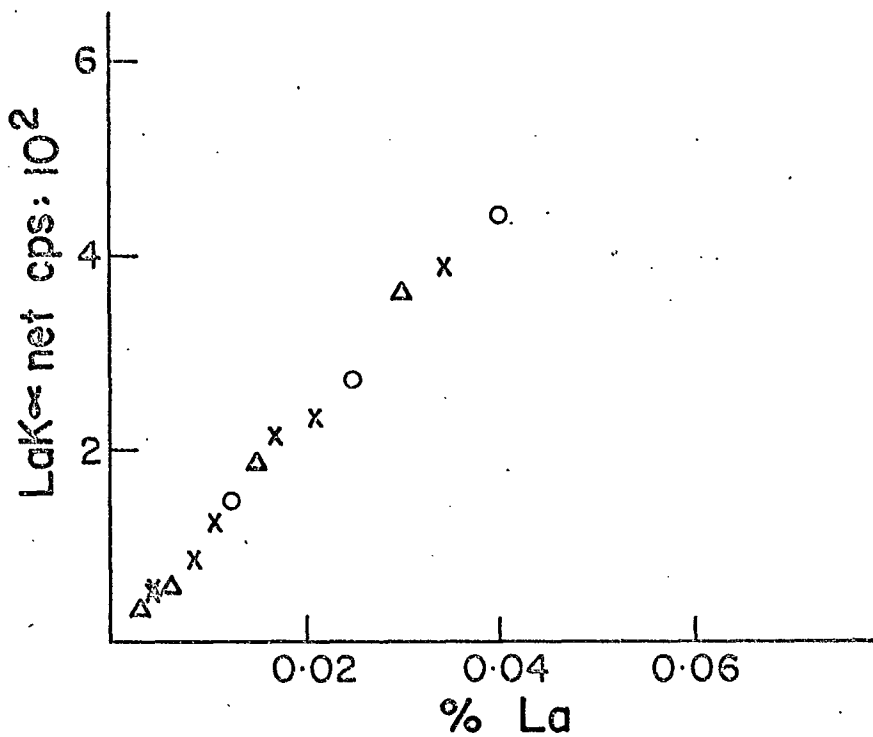and LaKα with 725 V to the Scintillation
Counter.

Figure 6: Counts for LaKa (top) and CeKa (bottom) from
Synthetic Standards using 11.6° background.