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**THE DETERMINATION OF SMALL AMOUNTS
OF ZIRCONIUM IN STEELS
BY X-RAY SPECTROGRAPHY**

by

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MINERAL SCIENCES DIVISION

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Dorothy J. Reed^{*} and A.H. Gillieson^{**}

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INTRODUCTION

There is what may be termed a "no man's land" in the determination of certain elements in specific materials - amounts too small to be determined readily by wet chemical procedures and at the same time too large for standard emission spectrographic techniques. The belief that X-ray spectrography could be useful in such areas was one reason for acquiring a 100 kv unit.

One specific problem included in these considerations was the determination of minor constituents in steels; in particular Zr, Nb and Mo up to a few tenths of a per cent. Zr was the first of such elements for which analysis was requested. Because all atomic X-ray phenomena are functions of the atomic number, problems arising in Zr determination should be similar to those that might be encountered with Nb and Mo as these follow Zr in the periodic table.

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STANDARDS

For the present purpose four of the NBS low alloy steel standards were suitable and had the following significant composition:-

	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>	<u>Sn</u>
1162	0.063	0.096	0.080	0.066
1163	0.200	0.195	0.120	0.013
1164	0.010	0.037	0.029	0.043
1167	0.094	0.290	0.021	0.100

These were sold as emission and X-ray standards, but they proved on receipt to be too thick for the Philips 60 kv sample chamber and too small in diameter for the sample containers supplied with the Philips 100 kv spectrograph. It was possible to scan these standards qualitatively by supporting them on mylar in the window of the sample holders of the 100 kv unit. However, for quantitative work exact positioning with regard to the X-ray beam is critical. Formerly small and odd-shaped samples had been given uniform size by means of a lead mask on which they rested. Lead was not used in this case as $PbL_{\gamma(1)}$ appears at the sample 2θ angle as $ZrK_{\alpha(1)}$. For these standard samples a Pt mask was made from a crucible cover.

DISCUSSION

In routine X-ray steel analysis for major constituents using solid samples, it has been general practice to use standards of a composition similar to the sample since inter-element effects occur, e.g., Cr radiation is affected by the amount of Mn, Fe and Ni present. To each analysis corrections for the other major constituents must be applied by one means or another.

In determining minor constituents in steels it was hoped that the Fe would act in the same manner as SiO_2 in the SiO_2 dilution technique for ores. In this procedure a 2% mixture of the ore in SiO_2 is prepared for analysis and it has been found that, under these conditions, 30% of neighbouring elements such as Ni, Cu and Zn in the ore fraction, does not interfere with the determination of the others, (1). A concentration of 30% of an element in an ore is equivalent to 0.6% in the final mixture. Assuming steels to be Fe dilutions analogous to SiO_2 dilutions, it should be possible to determine up to 0.5% of light components directly except in cases of line interference. For greater concentrations, corrections for inter-elemental effects must be considered. The dispersion of impinging X-rays by analyzing crystals is such that the resolution of lines of neighbouring light elements is better than that of heavy elements. Thus the estimation of Zr in the presence of Nb and Mo might be limited to less than the above 0.5% because of its high atomic number.

INVESTIGATIONS

A count scan was made on two of the standards over the 2θ range involved (Fig. 1). By making a count scan, small peaks and peaks no higher than the normal excursion of the pen on the recording chart can be magnified. The sloping background in the figure is normal. It is caused by the slope in the continuum from the X-ray tube as it approaches its maximum intensity near its short wavelength limit. The characteristic radiation of the elements is superimposed on this slope.

Because of this background slope and the proximity of neighbouring peaks, it was not possible to take background counts in the usual way by counting one or both sides of the K_{α} peak. The background at angles less than that of the peak could not be measured until well below the MoK_{β} peak and the effect of the intervening peaks on such a count could not be estimated readily. The best approach seemed to be measurement of the background at several angles above the ZrK_{α} peak. Then, by plotting these points and extrapolating the resultant line, the true background under the peak could be determined.

The profile and height of the continuum maximum is influenced by several factors other than the kv applied to the X-ray tube. Two of these factors that are readily altered and controlled are the voltage to the detector and the amplifier gain applied to

the signal from the detector. To determine the slope, pure Fe was scanned at 75 kv and 20 ma excitation while the detector voltage, amplifier gain and baseline were varied. Some of the tracings obtained have been transferred from the recorder chart and are shown in Fig. 2. The Mo peaks originate from the stainless steel sample holder. The most uniform slope was obtained with a potential of 1000 v on the scintillation counter, an amplifier gain of 50 and a baseline of 6 v. However, the background was high (the line has been plotted at half intensity) and the signal to noise ratio was poor. A change to 12 v baseline decreased the background significantly, but the slope was not as uniform as that produced when the amplifier gain was changed to 10 in addition. The 700 and 850 v tracings have been displaced downward by 10 divisions to separate them from the "1000 v, amp 10" records. They had the same slope as the best 1000 v tracings but the sensitivity was slightly less. The best conditions for background determination seemed to be 1000 v to the counter, amplifier gain 10 and baseline 12 v.

The 1000 v detector setting resulted in counts being taken just above the plateau of the scintillation counter, hence counts on different days might not be reproducible. However, the Pt mask, due to its origin, did not fit the holder properly and its position would alter from day to day (unless work was being done on this problem exclusively) and affect the counts also. With only four standards, a daily reference line was quickly established.

Thus far investigations had been carried out assuming low alloy steels could be regarded as iron dilutions for purposes of analysis. While there was a theoretical basis for this, there was no experimental evidence to support it. Preliminary X-ray results gave slightly higher Zr figures than did the corresponding emission results. The NBS standards contained Nb and Mo in addition to Zr, while the test samples did not. It was possible that the Nb and Mo could have absorbed part of the lighter Zr radiation and thus reduced the Zr counts causing the same amount of Zr to give fewer cps in the standards than in the samples.

To determine if the Nb and Mo in the NBS standards affected the Zr counts, pure Zr was added to eight 10 g portions of electrolytic Fe to give concentrations from 0.002 to 0.45% Zr. These binary standards were dissolved in HCl and HF and taken to dryness. The residue was ground to pass 200 mesh. Lathe turnings from the test samples were treated similarly. Portions of three of the resultant powders were submitted for X-ray diffraction analysis. They showed the presence of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, FeOCl and Fe_2O_3 . All were dried overnight at 150°C and stored in desiccators. Because of the powdered state of these samples and the absence of neighbouring element peaks, the best conditions for Zr determination were found to be 900 v to the scintillation counter with an amplifier gain of 50 and a baseline setting of 6 v. At 900 v a portion on the counter plateau was obtained so that results from day to day were expected to be

reproducible, being affected only by any variation in the equipment settings.

PROCEDURES

1. Solids

Using a Pt mask to achieve a uniform area of irradiation, samples and standards were counted at 75 or 90 kv and 20 ma with 1000 v to the scintillation counter, an amplifier gain of 10 and a baseline of 12 v. Counts were made at 22.55° 2θ LiF, the $ZrK_{\alpha(1)}$ peak, and at 23.50 , 24.00 and 24.50° for the background. On the samples background counts were also taken at 25.00° . Standards could not be counted here due to the presence of Sn. By extrapolation of the background counts, the background at 22.55° was estimated and subtracted from the peak counts to give net ZrK_{α} counts.

2. Powders

The powders, obtained from the samples and synthetic standards as outlined above, were counted at 80 kv and 20 ma using 900 v to the counter, an amplifier setting of 50 and a baseline of 6 v. Counts were made at the ZrK_{α} peak with background counts at 21.00 and 24.10° 2θ LiF. The powders were supported on a mylar film. No special packing or briquetting techniques were used. The mean of the background counts was subtracted from the peak count to give net Zr counts.

For both types of sample 96,000 counts were accumulated for the peak and 48,000 for the backgrounds.

RESULTS

Solid samples were analyzed on October 27 at 75 kv and on the following day at 90 kv. There was very little difference in results. As expected, there was slightly greater sensitivity at the higher kv. On January 25 analysis at 90 kv was repeated. At this time a source collimator with 0.005 in. spacing instead of 0.010 in. was used. Both peak and background counts were greatly reduced while the slope of the standard line more than doubled. As is shown in Tables 1 and 2, the mean difference in results was not significant.

While regression lines from four standards only are of no great value, the comparison of two from identical standards may be permissible. The earlier line was $Y = 0.000041X - 0.0007$ and had a correlation of + 0.9993 and a standard error of ± 0.004 . From the January counts the equation was $Y = 0.000095X + 0.0002$, the correlation + 0.9997 and the standard error ± 0.003 .

Powder samples were counted December 19 and January 23 with the same collimation for both. There was no significant difference in net counts between the two days. The results are given in Table 1. The mean differences in Table 2 showed no greater difference between solid and powder samples

than between repeat analyses on the solid ones.

The regression line for the 16 values obtained from the 8 powder samples counted on two different days was calculated. The equation was found to be $Y = 0.000114X - 0.009$, the correlation $+ 0.9994$ and the standard error ± 0.006 .

The mean difference between powder and solid samples was not significantly different from the standard errors of prediction, but it may be significant that in all but one instance, where the difference was zero, the powder samples gave lower results. With only 9 samples analyzed, this divergence cannot be considered established. Should future samples give similar results, the absorption of Zr radiation by Nb and Mo in low alloy steels, though slight and in many cases insignificant, will have to be considered.

In six cases X-ray and emission spectrographic results agreed completely or within the limits of X-ray error (Table 2). In the other three instances the differences are large. The difference in 23AN cannot be explained readily. Samples 24B and 24BN lie beyond the NBS standard range. The emission results are based on these standards only, therefore their reliability above the 0.2% range of Zr has not been established.

CONCLUSIONS

Zr in steels from 0.002 to 0.30% may be determined satisfactorily by X-ray spectrography without correcting for other minor constituents. It should be possible to extend the range below 20 ppm by the accumulation of more counts and by special sample preparation.

The reproducibility of daily settings of the controls on the 100 kv spectrograph is satisfactory for this determination.

PROJECTION OF WORK

In addition to indicating an approach to the determination of other minor constituents in steels, this investigation has introduced the possibility of overcoming inter-elemental effects between major constituents by dilution of the sample with electrolytic iron. Thus major constituents would be reduced to the level of minor ones and determined similarly. The effect of dilution would have to be determined as SiO_2 dilution has indicated that it is probably not a simple arithmetic factor.

REFERENCE

1. Reed, D.J. and Inman, W.R., Silica Dilution in X-ray Fluorescence Analysis of Ores and Mineral Dressing Products. Ottawa Symposium on Applied Spectroscopy, September, 1958. (unpublished).

TABLE 1

Per Cent Zr in Steels by Different Methods

Sample Number	X-ray Results			Emission Results (a)
	Solids-90 kv (a)		Powders (b)	
	Oct	Jan	Dec + Jan	
19	--	--	--	<0.001
19A	0.025	0.026	0.015	0.015
19B	0.003	--	--	<0.001
23	--	--	--	<0.001
23A	0.076	0.086	0.071	0.071
23B	0.008	0.010	0.009	0.004
23N	--	--	--	<0.001
23AN	0.077	0.084	0.072	0.043
23BN	0.008	0.007	0.002	0.002
24	--	--	--	<0.001
24A	0.039	0.042	0.035	0.032
24B	0.342	0.382	0.320	0.234
24N	--	--	--	<0.001
24AN	0.048	0.040	0.028	0.019
24BN	0.327	0.355	0.340	0.242

(a) vs NBS standards.

(b) vs synthetic standards.

TABLE 2

Differences in Results

Sample Number	X-ray Results		Powder - Emission
	Oct - Jan	Solid - Powder	
19A	- 0.001	+ 0.010	--
23A	- 0.010	+ 0.010	--
23B	- 0.002	--	+ 0.005
23AN	- 0.007	+ 0.008	+ 0.029
23BN	+ 0.001	+ 0.006	--
24A	- 0.003	+ 0.005	+ 0.002
24B	- 0.040	+ 0.042	+ 0.086
24AN	+ 0.008	+ 0.016	+ 0.009
24BN	<u>- 0.028</u>	<u>+ 0.001</u>	<u>+ 0.098</u>
Mean	- 0.011	+ 0.011	+ 0.026

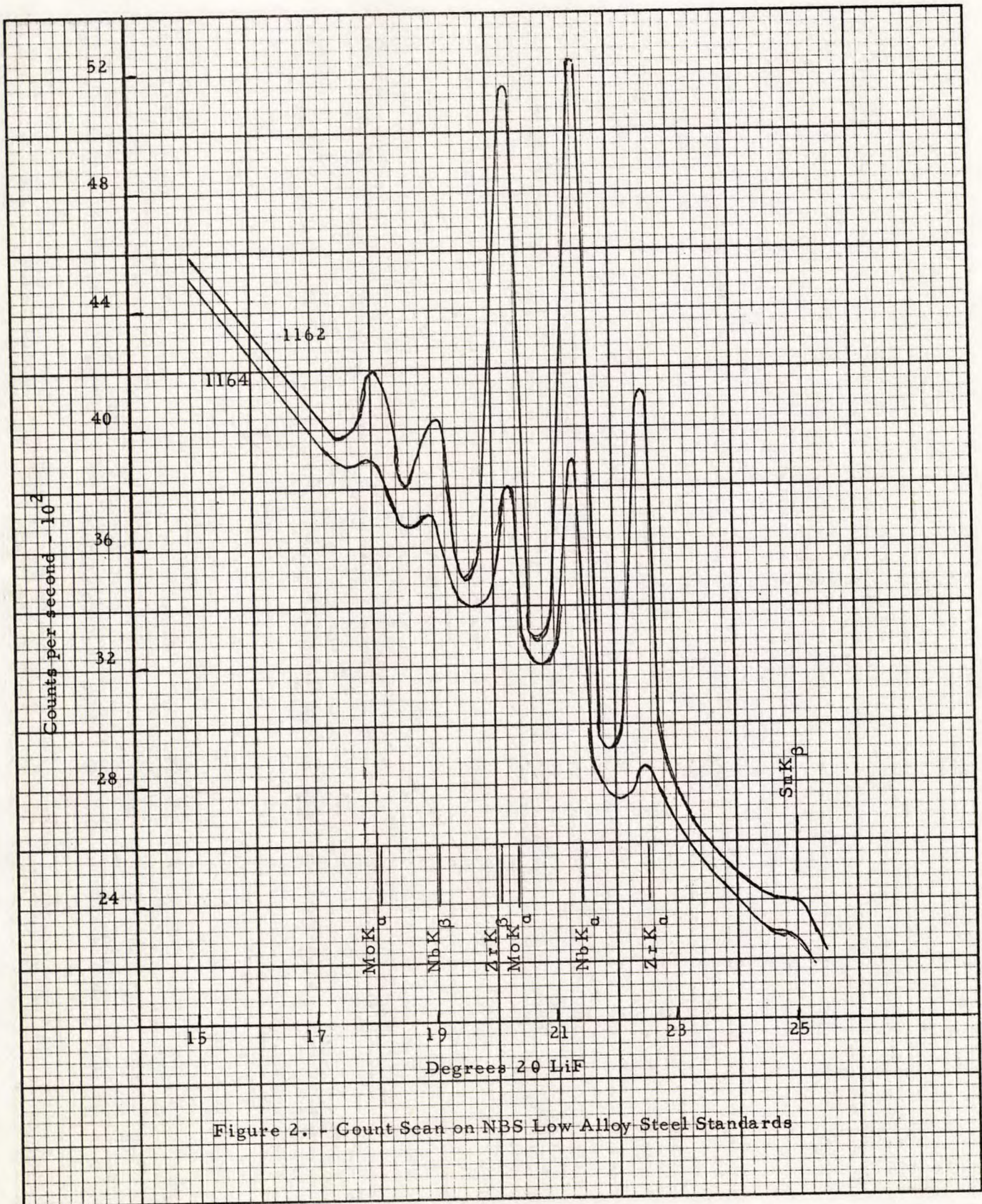


Figure 2. - Count Scan on NBS Low Alloy Steel Standards

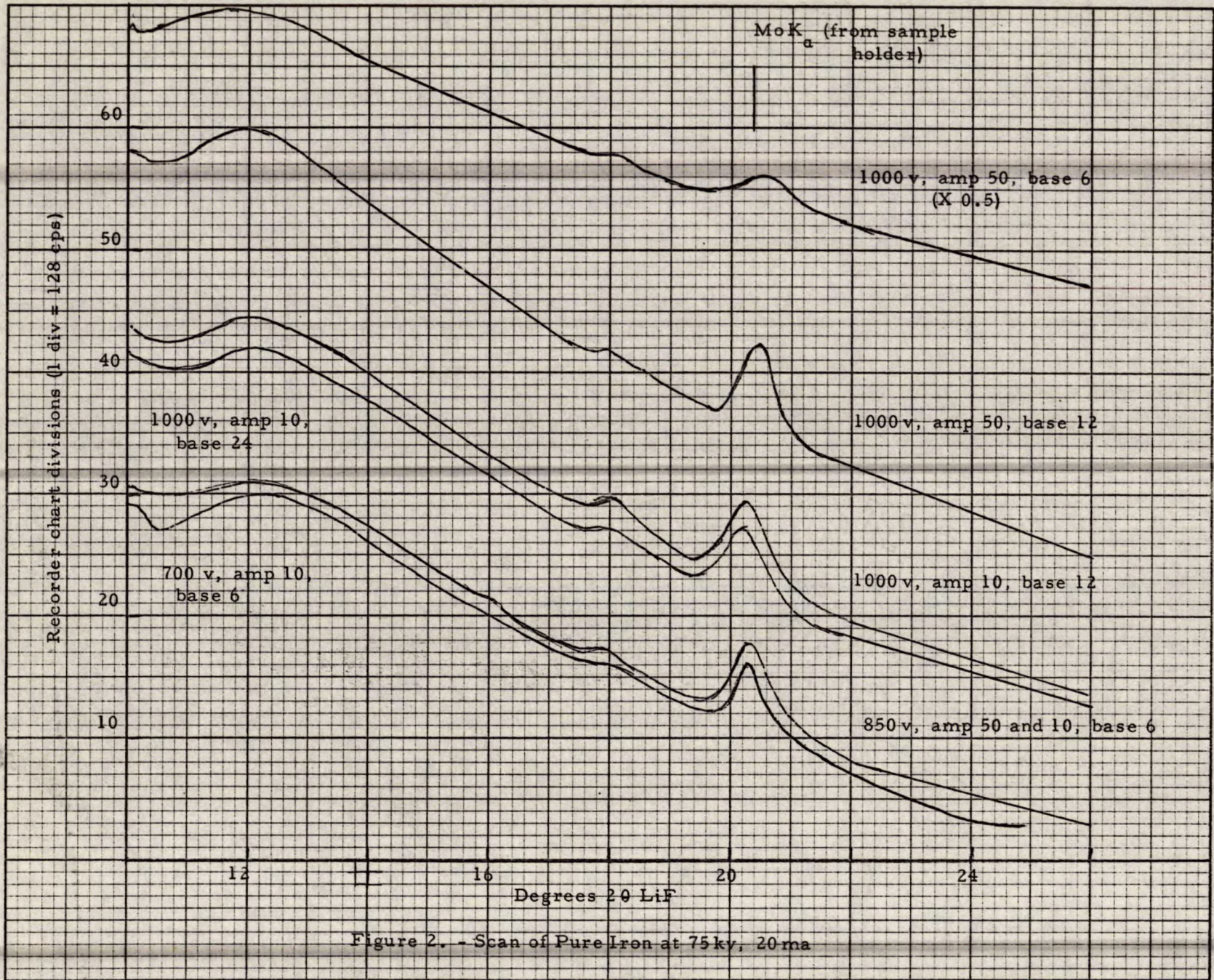


Figure 2. - Scan of Pure Iron at 75 kv, 20 ma