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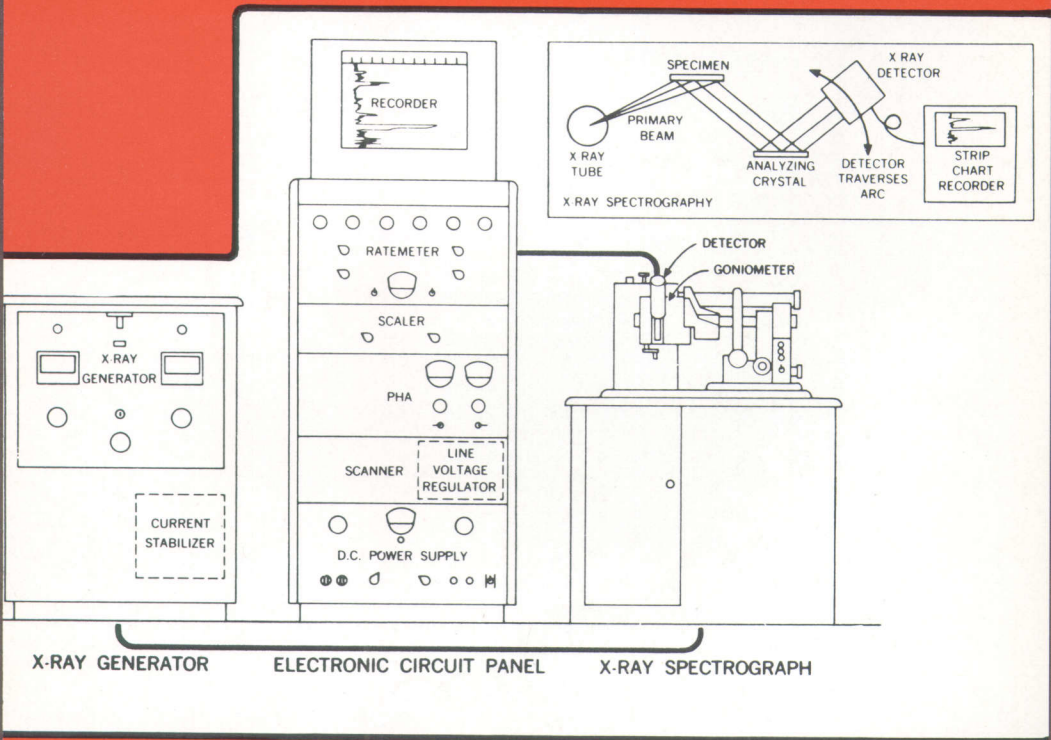
X-RAY SPECTROSCOPIC ANALYSIS of SIX MINERAL ELEMENTS in WOODY TISSUES



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X-RAY SPECTROSCOPIC ANALYSIS OF SIX MINERAL ELEMENTS IN WOODY TISSUES[1]

By

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INTRODUCTION

X-RAY SPECTROSCOPY as a means to quantify certain elements in plant tissues has been utilized infrequently in recent years, although other materials have been examined routinely using this technique. X-ray spectroscopy offers certain advantages over other methods of analysis, such as: (1) manner of analysis, (2) ease of sample preparation, and (3) non-destruction of samples during analysis.

A portion of this investigation was to determine whether quantitative differences existed between certain chemical elements in figured and unfigured wood. Such differences were sought as a basis which might be utilized to elucidate initiation and formation of figured wood in certain trees *(1)*.

X-ray spectroscopy was selected to determine whether satisfactory analysis of woody tissues could be obtained by this technique as compared to published analyses achieved by more conventional techniques. This report presents calibration information concerning calcium, copper, iron, nickel, potassium, and zinc and includes quantitative analyses of these elements in woody tissues as determined by x-ray spectroscopy. This information should be useful to other investigators utilizing this technique for plant tissue analyses.

[1] Research was supported by McIntire-Stennis Research Funds as Project No. 914 and constituted a portion of a thesis for a MS degree for the senior author *(9)*.

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LITERATURE REVIEW

Several researchers, utilizing x-ray spectrographic analysis methods for certain elements in plant materials, have reported comparable results to chemical methods. Whittig *(11)* obtained a variability of 1.6 ppm in plant tissue analysis for zinc by employment of a select scatter wavelength as a standard of comparison. Whittig used an LiF analyzing crystal to measure KA radiation of zinc at 41.8 degrees and scatter at 41.0 degrees. For calibration of zinc, Whittig employed additions of zinc to the plant material being analyzed to serve as standards. Dixon and Wear *(3)* followed procedures similar to those of Whittig in an analysis of plant material for manganese, iron, copper, and zinc; their results were comparable to those obtained by chemical methods. In analyzing for copper, Dixon and Wear measured radiation from the second order KB line of copper to avoid interference from the W:LAl line of the x-ray tube utilized. Dixon and Wear obtained a standard deviation of 2.14 ppm in analyzing for copper and 1.27 ppm for manganese in plant material.

Twenty three elements have been reported in wood in the basic matrix of carbon, hydrogen, and oxygen. These include boron, nitrogen, sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, silver, tin, thallium, and lead. Results reported by various researchers are given in tables 1 and 2, which show general agreement on relative amounts of elements reported. Principal elements in the matrix of wood are calcium, nitrogen, potassium, magnesium, phosphorous, manganese, and silicon; trace amounts of aluminum, boron, sulfur, chlorine, sodium, iron, copper, zinc, and molybdenum are present. With respect to other trace elements that occur in wood, no information was presented as to relative amounts present *(12)*.

Ash content of wood is approximately 0.2 to 0.9 percent of dry weight and is quite variable for different species and within specific species; there also is some variation with respect to growing conditions and season of the year *(5)*. There is little agreement as to whether ash content of heartwood differs from that of sapwood; a similar situation exists concerning trunkwood and branchwood.

Certain tree species are characterized by inclusions of crystalline deposits in various tissue elements. Calcium oxalate is a

common crystalline deposit that occurs in vertical and ray parenchyma cells of both heartwood and sapwood of oak, hickory, walnut, and persimmon as well as other species *(5,7,12)*. Crystals of calcium oxalate are generally quite large and are referred to as "crystal sand" in a number of species. Calcium carbonate deposits occur in a number of hardwoods including elm, hackberry, and oak *(5)*. Generally, calcium carbonate deposits occur in vessels of heartwood, in and around knots, in and around heartwood induced by injury (pathological heartwood), and in the pith; rarely is calcium carbonate detected in normal sapwood *(12)*. The middle lamella (amorphous intercellular layer) between wood

TABLE 1. DRY-WEIGHT LEVELS OF ELEMENTS REPORTED IN PLANTS BY VARIOUS WORKERS *(2,5)*

Element	Range in ppm	
	Low	High
Al	2	10,000
B	<5 (normally 10)	>1,500 (normally 100)
Ca	<1,000	>10,000
Cl	2,500	10,000
Co	<0.01	1.0
Cu	1	>25*
Fe	20	several hundred
Li	fraction	10**
Fl	1	100
Mg	500	10,000
Mn	5	1,000
Mo	0.01	25 or more
N	2,000	40,000
P	300	3,000
K	200	35,000
Na	100	10,000
S	1,000	10,000
Zn	5	75

* Where copper sprays had been used.
** Dry citrus leaves.

TABLE 2. DRY-WEIGHT LEVELS EXTRAPOLATED FROM A STUDY BY SCHNEIDER OF SIX BLACK WALNUT STEMS FROM TREES 4.4 TO 7.0 INCHES dbh *(8)*

Element	Amounts in ppm		
	Largest tree	Smallest tree	Average tree
Na	27.7	66.2	21.5
Mn	0	0	5.4
Fe	9.1	8.7	17.5
Cu	3.0	1.6	4.9
B	9.3	3.2	2.9
Zn	2.8	0	6.6
Al	0	13.0	4.0

cells is composed largely of calcium pectate *(7)*. In sugar maple, the insoluble material separated from the sap in making syrup is calcium malate or "sugar sand" *(5)*. Siliceous inclusions have been observed in ray and vertical parenchyma cells, fiber elements, and vessels of certain species *(12)*.

MATERIALS AND METHODS

Specimen and Internal Standard Preparation

The characteristically figured woods chosen for study (Claro walnut, black walnut, and bigleaf maple) were obtained from California as air-dried cross sections from top and butt ends of export logs. A sequential series of 1-inch cubical samples were removed from each cross section starting at the pith and extending radially to the bark. Fractional portions remaining after the last whole cube was measured were left attached to that measured cube and considered as a sample. Bark was removed from all samples and discarded.

Each sample was split, visually classified as to figure type, and then ground in a Wiley mill to a fine powder to pass through a 60-mesh monel screen. Two grams of wood powder from each sample were pressed into a pellet under a load of approximately 400 psi. A plastic backing was pressure formed with the wood powder pellet. A pellet of 2 grams of dry wood tissue had been determined by preliminary tests to be optimum to the depth of primary x-ray penetration. Pellets were 1.25 inches in diameter, 0.375 inch in thickness, and had a total weight of approximately 4 grams. Excess powdered wood was accumulated, mixed, and used to determine moisture content for the species examined.

Internal standards for a given element were prepared from selected sections of non-figured walnut or maple. Wood tissue for internal standards was ground in the same manner as described for the sample specimens. Wood powder of selected sections of walnut or maple was mixed thoroughly in a sterile polyethylene bag to ensure homogeneity. Part of the powder was used for moisture content determinations and part saved for preparation of reference specimens (without addition of internal standards). Internal standards were prepared in similar fashion to sample specimens. Two grams of wood powder from a single section of walnut or maple were placed into a small sterile polyethylene bag and wetted with acetone. An aliquot from a standard

solution that contained the element desired for calibration was pipetted into the wetted wood tissue and thoroughly mixed with a plastic stirrer until most of the acetone had evaporated *(11)*. Internal standards were dried in a forced-draft oven at 65°C and pressed into pellets identical to those described for the sample specimens.

Two internal standards were prepared for each added amount of all elements under investigation (one for walnut and one for maple). Range of additions was limited to ranges reported in literature for similar woods or, for lighter elements such as aluminum, to a concentration thought to be readily detectable. Furthermore, internal standards prepared were limited to elements for which a suitable standard solution could be purchased and that were within the fluorescing power of the available tungsten target x-ray tube. Elemental detection limits of the available x-ray tube confined analyses to elements from atomic number 13 through 55.

Adjustment of the X-Ray Spectrometer

The spectrometer was adjusted to the Bragg diffraction angle of the K doublet line for the element of interest and for the particular analyzing crystal employed. With a standard specimen of high concentration exposed to the x-ray beam, x-ray tube voltage and current then were adjusted to yield fluorescence of satisfactory intensity. The detector voltage was checked to ascertain that the detector was functioning well into the threshold plateau as well as rendering a maximum yield. A more nearly exact angle for the peak of the fluoresced line was determined for the detector and analyzing crystal relationship by scanning through the region adjacent to the Bragg diffraction angle.

The above preliminary adjustment was accomplished with the amplifier gain set at midrange and the pulse height analyzer set to differentiate between energy distributions. To eliminate excessive noise, the analyzer circuit baseline was set at 3 volts when the proportional counter was in use and at 6 volts when the scintillation counter was in use. The window of the pulse height analyzer circuit was maintained at 15 volts or higher.

Detector voltage was adjusted to yield the highest intensity while most frequent pulses were limited to about 9 volts in order to minimize generation and counting of unwanted noise. For scintillation counter operation, amplifier gain was adjusted until

the optimum F/S ratio was achieved. This adjustment sometimes necessitated readjustment of detector voltage. Amplified gain was maintained at midrange for proportional counter operation.

Pulse amplitude distribution (PAD) of the line under study was plotted by the strip chart recorder while scanning the baseline downward from a maximum of 60 volts with the window set at 3 volts. In proportional counter operation, baseline and window were set to accept only those pulses within a 90 percent probability area under the normally distributed PAD curve as graphed by the strip chart recorder. Baseline and window settings were adjusted to incorporate the 90 percent area by setting the window to reject any pulses one-half an amplitude higher than the most frequent pulse and the baseline to reject any pulses more than one-half amplitude lower than the most frequent pulse *(6)*. For scintillation counter operation, baseline was adjusted to eliminate dark current from the photomultiplier tube, usually a 6-volt setting was sufficient, and the window was set to maximize the F/S ratio. The ratio usually was maximized by a window setting including the 60 percent probability area under the PAD curve already determined. Analysis using the proportional counter was accomplished with amplified gain set at midrange, but for scintillation analysis, amplifier gain was more critical and was adjusted to maximize the signal to noise ratio. Table 3 indicates x-ray unit settings employed in analyses.

Calibration Technique

Calibration interferences can be compensated by building internal standards for the element in question. In this procedure, internal standards are prepared by adding amounts of the elements in question to the material to be analyzed and determining a particular wavelength of scatter for a standard of comparison.

TABLE 3. X-RAY UNIT SETTINGS EMPLOYED IN ANALYSES OF WOOD SAMPLES

Element	K	Ca	Fe	Ni	Cu	Cu	Zn
Line	KA	KA	KA	KA	KA	KB	KA
Counter voltage	1485	1485	810	810	830	830	830
X-ray tube, kv/ma	45/35	40/35	45/35	40/35	45/35	45/35	50/40
Peak, ° 2Θ	20.36	15.08	57.4	48.37	44.91	40.4	41.6
Background ° 2Θ	24.60	13.00	54.5	47.60	44.10 45.70	39.7 41.1	40.8
Proportional Counter PET Analyzing Crystal Amplifier Gain Set at Midrange (50)			Scintillation Counter LiF Analyzing Crystal				

In theory, fluorescent yield from an added amount of an element should be influenced by interference in a similar manner as the fluorescence from the amount present, when the amount added is approximately the same as the amount present. An amount added beyond the range of amount present may yield different interference effects.

By selecting a scatter wavelength close to the elemental line of interest, absorption of scatter wavelength should be very similar to that of the line. In this way, the ratio of the line fluorescent yield to scatter intensity should be constant per unit of the element in question and, when so, will be established by linearity of the calibration curve. Similar materials or matrices should yield about the same level of scatter and the same F/S ratio per unit of element present. Conversely, different materials usually have dissimilar levels of scatter; therefore, F/S ratios per unit of a given element would not be the same. Starch and clear plexiglass (assuming that they possess matrices similar to wood) were used to determine the F/S ratios for zero concentration intercepts of calibration curves.

Interference from the characteristic and contamination lines of the x-ray tube was considered in calibration. To determine the presence of these lines, diffraction regions adjacent to the line of interest were scanned using a sample of clear plexiglass. Plexiglass has a light elemental matrix of carbon polymers and yields little fluorescence with a high intensity of primary radiation scatter. Therefore, plexiglass is a good source of scatter for adequate detection of interference lines.

Once a calibration curve based on F/S ratios is determined for a given element, matrix, and operating conditions, it is unnecessary to reestablish the calibration curve for each day of operation unless there is a change in the F/S ratio. All elements analyzed with the scintillation counter in this study were calibrated on F/S ratios. Conversely, all elements calibrated with the proportional counter were either based on the peak intensity where scatter was less than 5 percent of peak intensity or on the peak minus scatter intensity where scatter was greater than 5 percent. For proportional counter operation, the determined calibration curve had to be reestablished for daily operation since there was no basis of comparison other than absolute intensities of peak and scatter.

With copper, where the peak of interest was located on the side of a greater peak, background was taken on both sides of the peak to give a better estimate of scatter intensity. Angles of scatter were chosen such that the average of their sums was equal or nearly equal to that of the peak angle.

RESULTS AND DISCUSSION

Results of this investigation relate to analyses of mineral elements in woody tissue with respect to analysis techniques employed, accuracy of measurements, and general data. For all elements considered in order of their atomic number, the following information is presented:

(1) Pulse height amplitude distribution curves to indicate energy resolutions obtained;

(2) An overall view of relative intensities of wavelengths diffracted in regions of peaks of elements considered;

(3) A critical view of regions of elements for sources of interference and relative amounts of elements present in woods analyzed;

(4) An examination of calibration curves, when applicable, obtained for elements; and

(5) A summarization of accuracy of measurements and amounts detected for elements, and a comparison of results with published data.

Angles, used in analysis and represented in figures, are not exactly those that would be predicted from Bragg diffraction angle tables for the analyzing crystal employed but vary from the predicted by small differences in the goniometer-analyzing crystal relationship. Limits of resolution given for those elements analyzed using the proportional counter represent a 95 percent level of confidence for the peak above a three sigma level of background. For those elements analyzed with the scintillation counter, limits of resolution represent a two sigma level of confidence of equal probability or maximum error for the peak to background ratio. A clear plexiglas scan is included for the region of elements to provide a critical comparison for interference sources. Scans utilizing either walnut or maple samples are intended to be representative of both woods.

RESOLUTION AND DETECTABILITY

Potassium and Calcium

The plexiglass scan obtained for the potassium-calcium region (Figure 1) shows a contamination line from potassium. Intensity level of the peak of the contamination line was taken to be an average background level in determining limit of resolution and estimating amounts of potassium present. Figures 2 and 3 show PAD curves and analyzing conditions used for potassium and calcium. Figures 4 and 5 illustrate the effect of pulse height discrimination on relative intensities of peaks of potassium and calcium. Noting that the scale factors of the two figures differ by one-half, it is apparent that peaks of each element are dampened by selective discrimination between energy distributions of the KA peak of potassium or calcium. However, peaks are too close in energies to be eliminated by selective discrimination. Since potassium and calcium are one atomic number apart, it is not possible to separate effects of mutual interference, especially that of the KB1 peak of potassium and the KA peak of calcium. Amounts of potassium and calcium present in walnut and maple were, as expected, quite large (as indicated by intensities of peaks in figures 4 and 5).

Figure 6 is the calibration curve determined for potassium. As shown, the walnut sample used for calibration yielded about 580 counts per second (cps) for 1,000 ppm added; maple yielded about 760 cps for 1,000 ppm added. Calibration curve slopes in Figure 6 are the same and indicate that matrices of walnut and maple are essentially the same with respect to potassium. Similarly, the calibration curve for calcium (Figure 7) shows matrices of walnut and maple are the same with respect to calcium. The maple sample produced about 1,090 cps on the calcium peak for 1,000 ppm added and the walnut sample produced 2,400 cps for 1,000 ppm added.

The resolution limit for potassium for a precision of 16,000 counts accumulated was determined to be 0.9 ppm for both walnut and maple, but the experimental variability for walnut and maple were different (56.4 ppm and 36 ppm, respectively). The resolution limit for calcium for a precision of 64,000 accumulated counts was 0.2 ppm for both walnut and maple. Experimental standard deviations for calcium were quite different for walnut and maple (98.6 ppm and 44.6 ppm, respectively). Differences

between limits of resolution and experimental variabilities for potassium and calcium are most likely a result of heterogeneity of amounts present, especially for calcium in walnut where it commonly occurs as large crystals of calcium oxalate.

The average amount of potassium was 545 ppm in walnut (ranging from 180 to 1,050 ppm) and 763 ppm in maple (ranging from 350 to 1,850 ppm). These averages and ranges agree favorably with those reported previously. Hawley and Wise (5) established the relative amount of K_2CO_3 in wood ash as 10 to 20 percent of dry weight; K_2CO_3 rarely occurred below 5 percent. Other researchers (2) indicated that a range from 2,000 to 35,000-ppm potassium might be expected.

The average amount of calcium was 1,957 ppm in walnut (ranging from 950 to 6,080 ppm) and 2,118 ppm in maple (ranging from 1,250 to 11,420 ppm). Amounts of calcium detected agree with those established previously. Hawley and Wise (5) indicated that CaO could be found in amounts of 60 to 78 percent of total dry weight of wood ash; rarely did it occur below 20 percent. Other workers (2) reported calcium in plant tissues ranging from 1,000 to over 100,000 ppm.

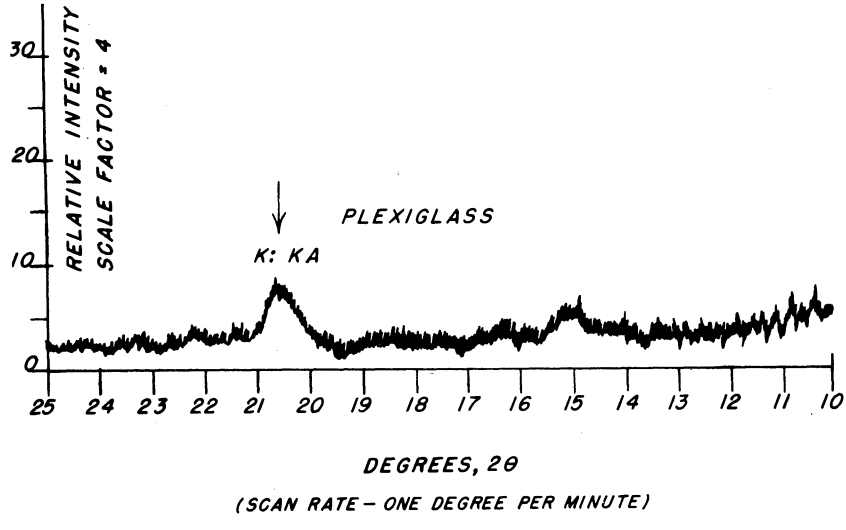

FIG. 1. Scan of potassium and calcium regions with clear plexiglass.

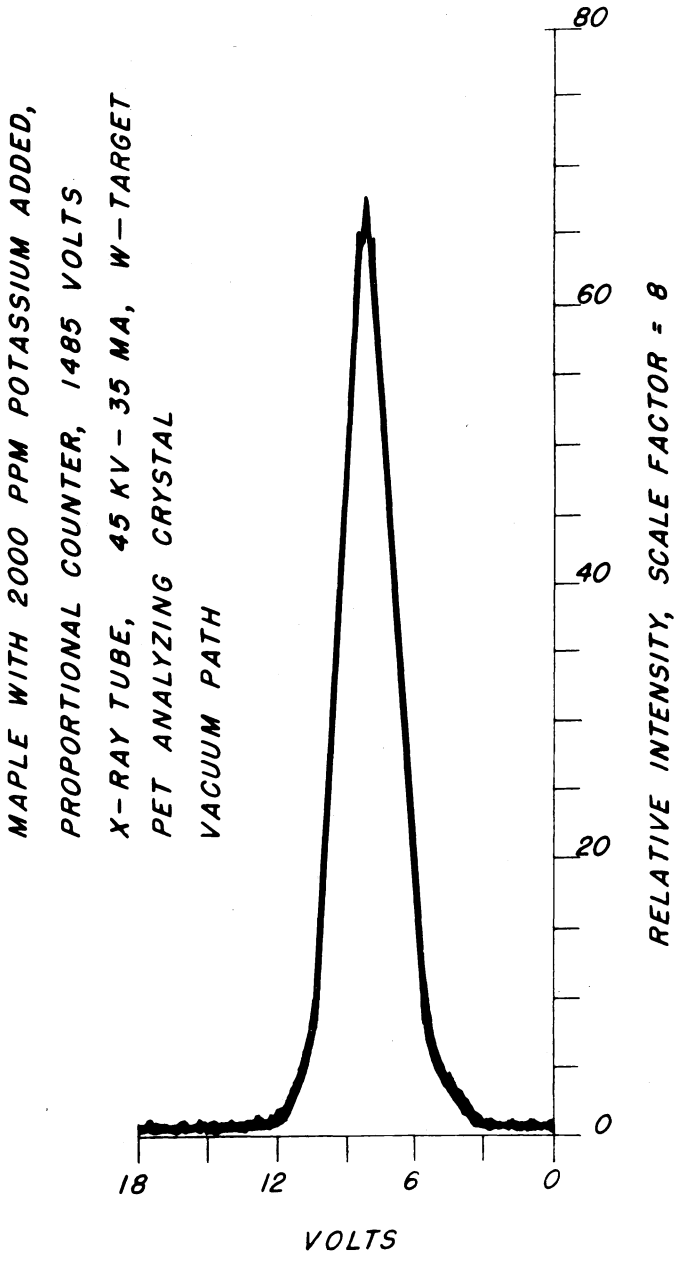

FIG. 2. Pulse height analyzer curve, potassium.

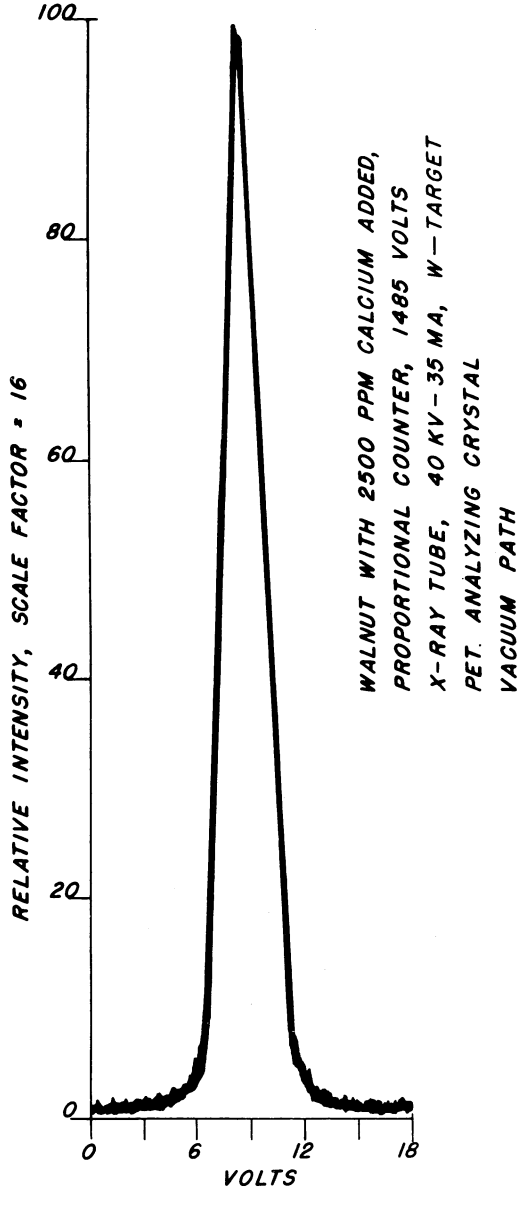

FIG. 3. Pulse height analyzer curve, calcium.

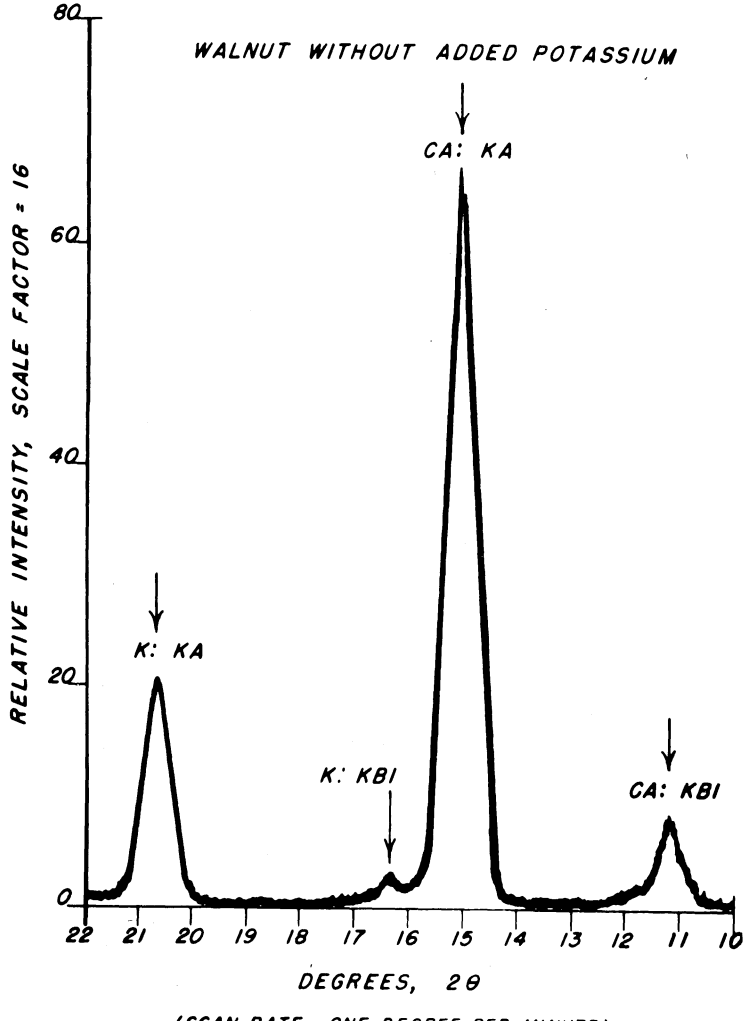

FIG. 4. Potassium in walnut or maple (discriminating against calcium).

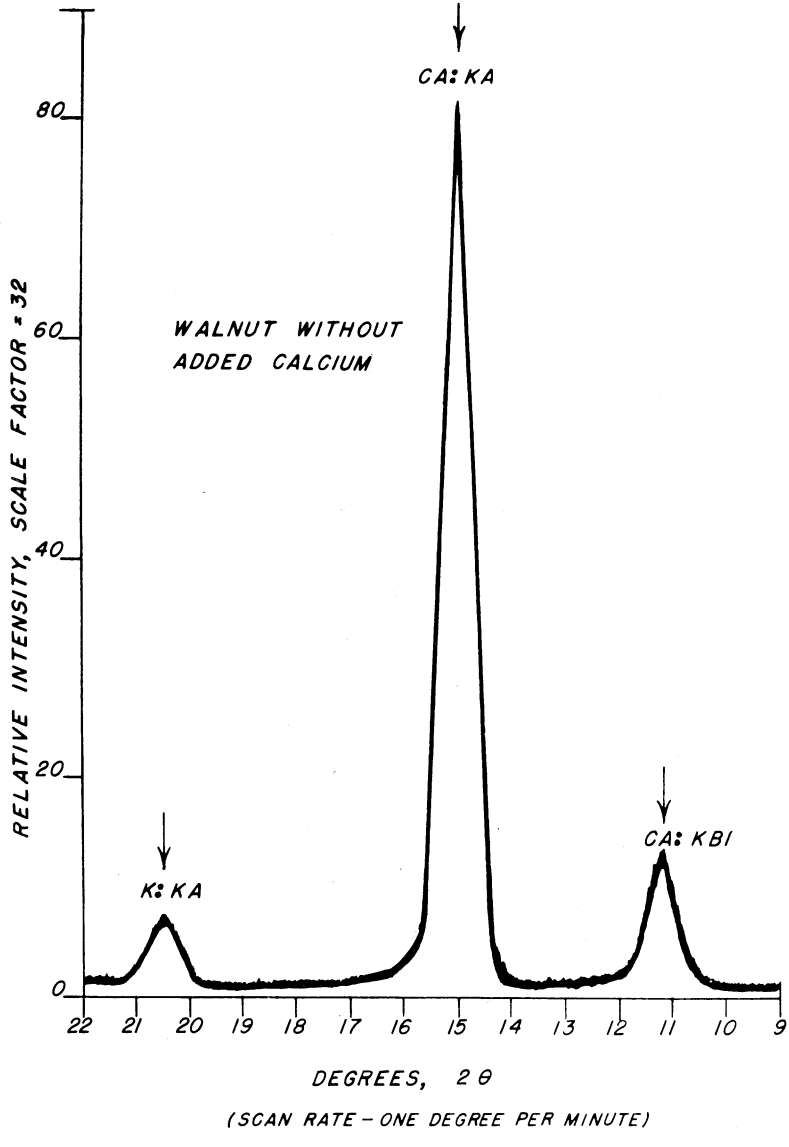

FIG. 5. Calcium in walnut or maple (discriminating against potassium).

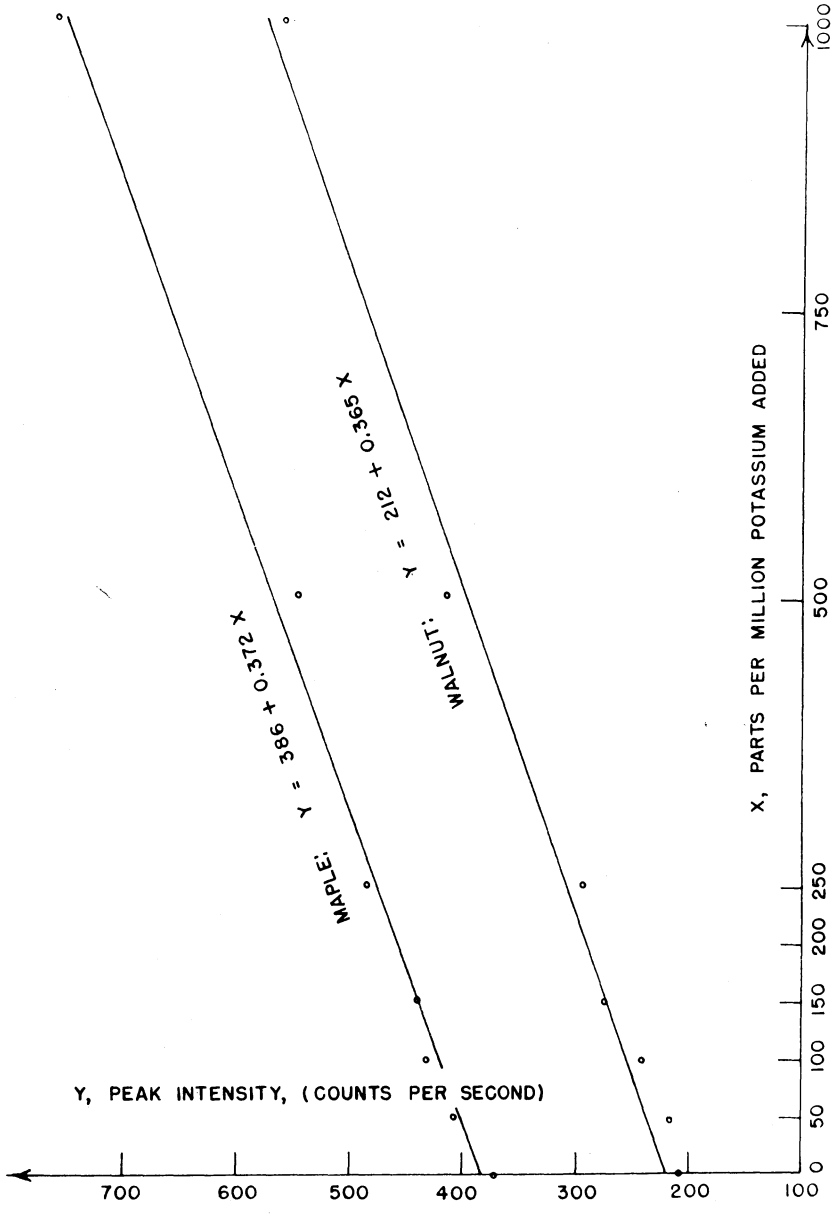

FIG. 6. Calibration curve for potassium.

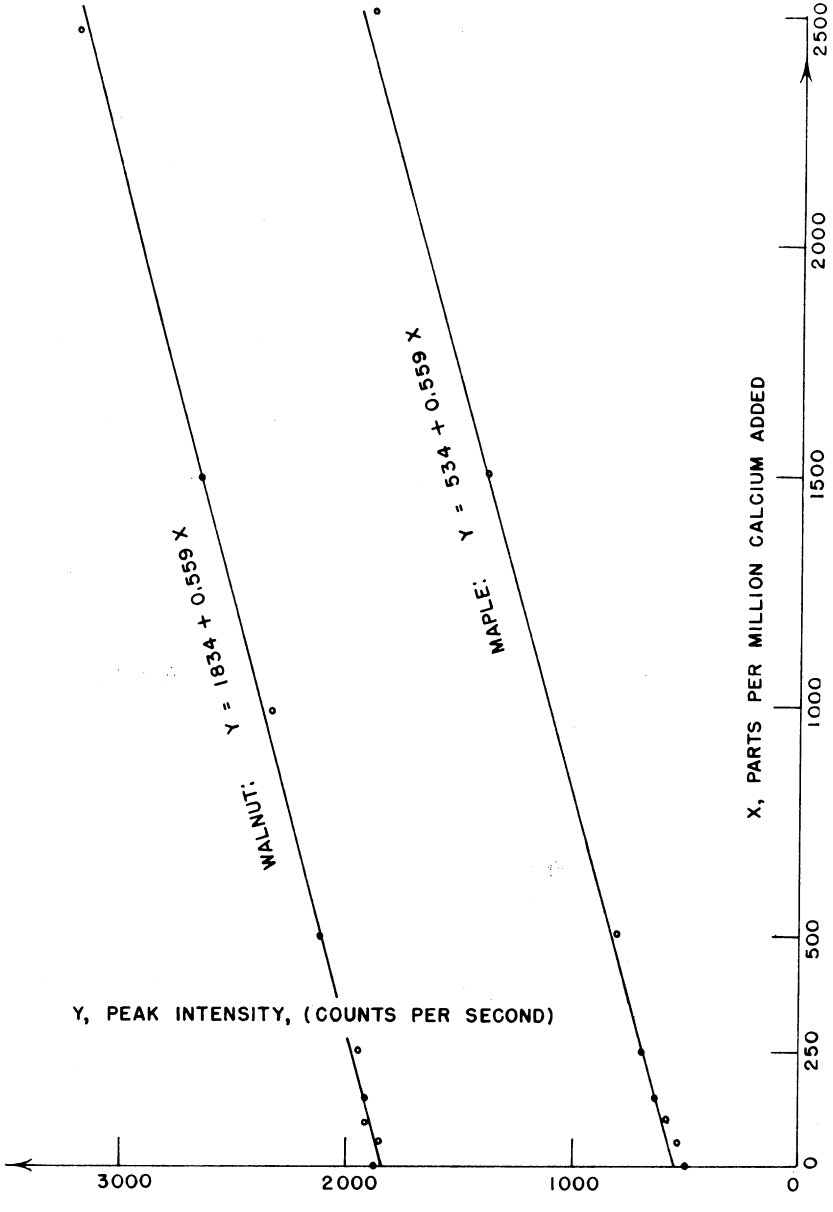

FIG. 7. Calibration curve for calcium.

Iron

The PAD curve and analyzing conditions employed for analysis of iron are shown in Figure 8. The region for iron is illustrated by Figure 9 and depicts no apparent sources of interference. However, more critical scans shown in Figure 10 indicates the iron KA peak on the downward sloping tail of the W:LA1 peak (located at 43 degrees). Amount of iron present in walnut or maple is demonstrated by Figure 10 (quite readily detectable). The calibration curve for iron in Figure 11 shows the iron present in walnut or maple to be well above the zero limit indicated by plexiglass (the starch standard was assumed to have iron contamination). The calibration curve for iron yields a ratio of 3.3 for 250 ppm iron added and 9.3 for 1,000 ppm added.

The resolution limit with 16,000 counts accumulated precision was 3.7 ppm and the experimental standard deviation was 2.2 ppm. Contamination from iron in grinding wood samples in a Wiley mill was considered to be in a magnitude of 2.0 ppm *(3)*.

Average amount of iron was 93.2 ppm in walnut (ranging from 20 to 198 ppm) and 70.8 ppm in maple (ranging from 12 to 141-ppm). Amounts of iron detected in walnut were much greater than those reported by Schneider *(8)*, who obtained a range of 8.7 to 17.5 ppm in black walnut. Other workers *(2,4,5,10)* indicate that the amount of iron will range from approximately 20 to several hundred ppm in plant material.

Nickel

The PAD curve for nickel is given in Figure 12, which shows a well distributed curve for the amount of nickel added. Scan of the nickel region (Figure 13) demonstrates the nickel KA peak on the tail of the W:LAl peak and on the side of the much smaller W:LL peak. More critical scans (Figure 14) show that the W:LL peak is the most critical interference for the analysis of small amounts of nickel. The relative amount of nickel present in walnut or maple was insufficient to be shown by the relatively rapid scan shown in Figure 14. Intensity of even a small amount of nickel is quite strong as shown by Figure 14 and especially so when the calibration curve for nickel (Figure 15) is considered. The curve gives a F/S ratio of 1.87 for 50 ppm added and 17.45 for 1,000 ppm added, which is about twice that obtained for iron (9.3 for 1,000 ppm added).

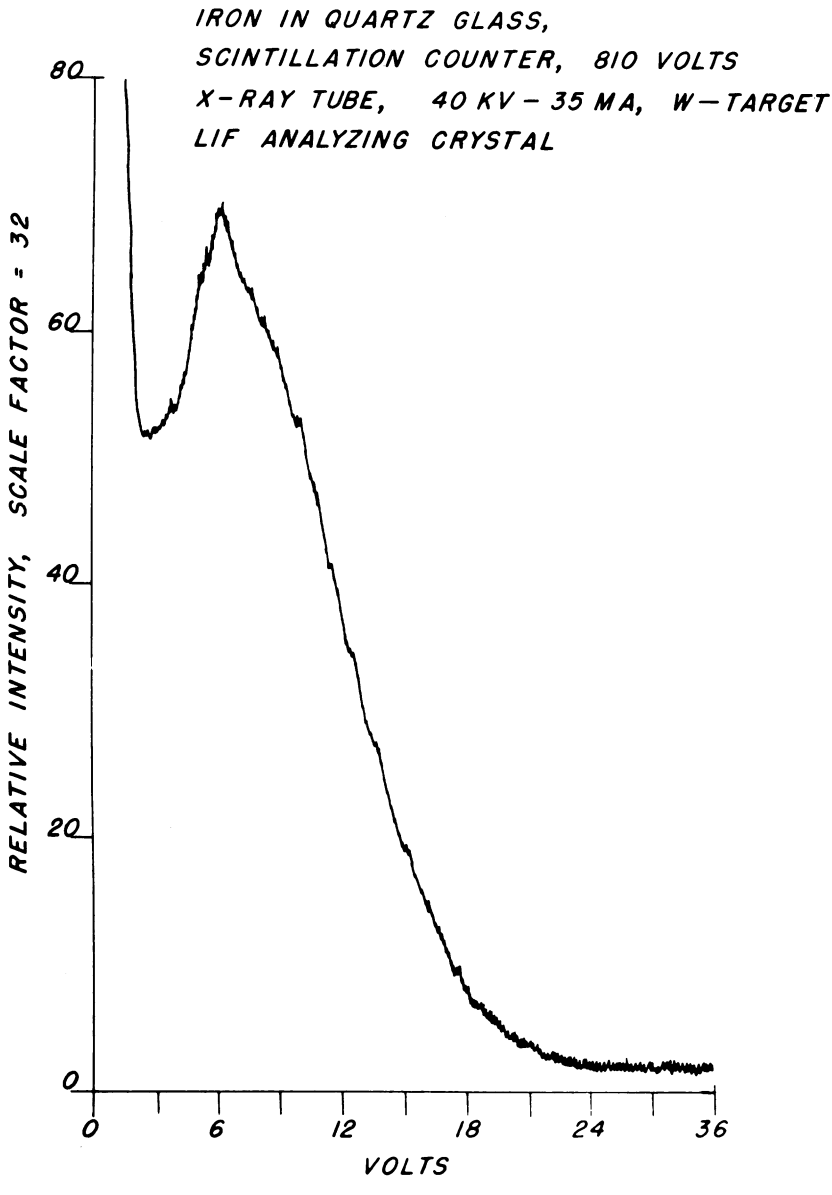

FIG. 8. Pulse height analyzer curve, iron.

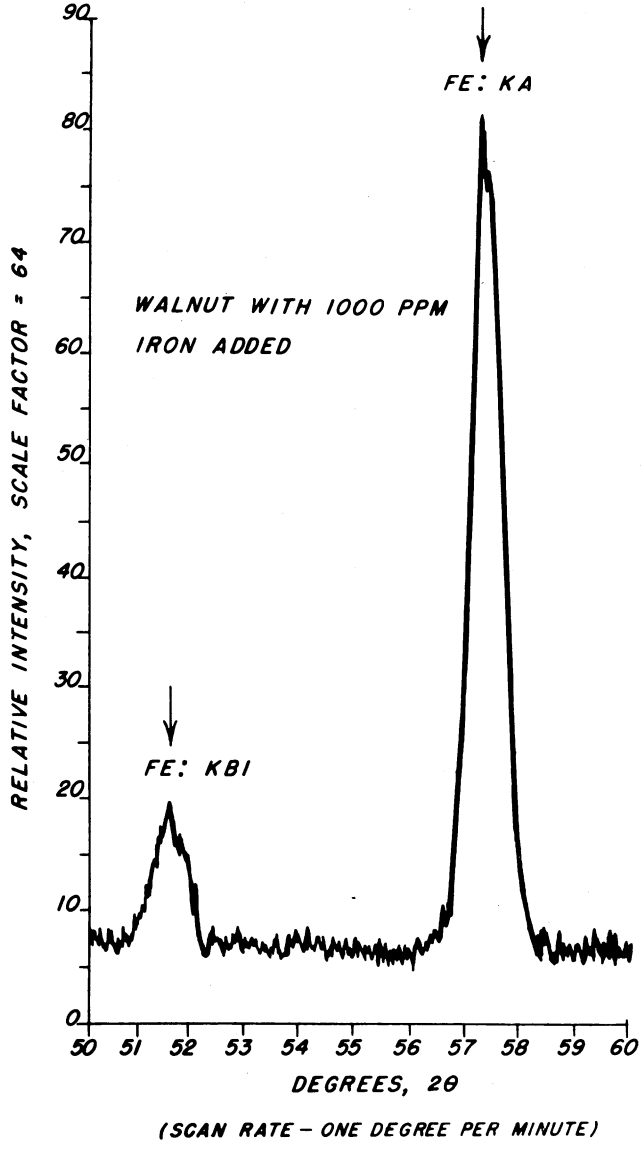

FIG. 9. The iron region.

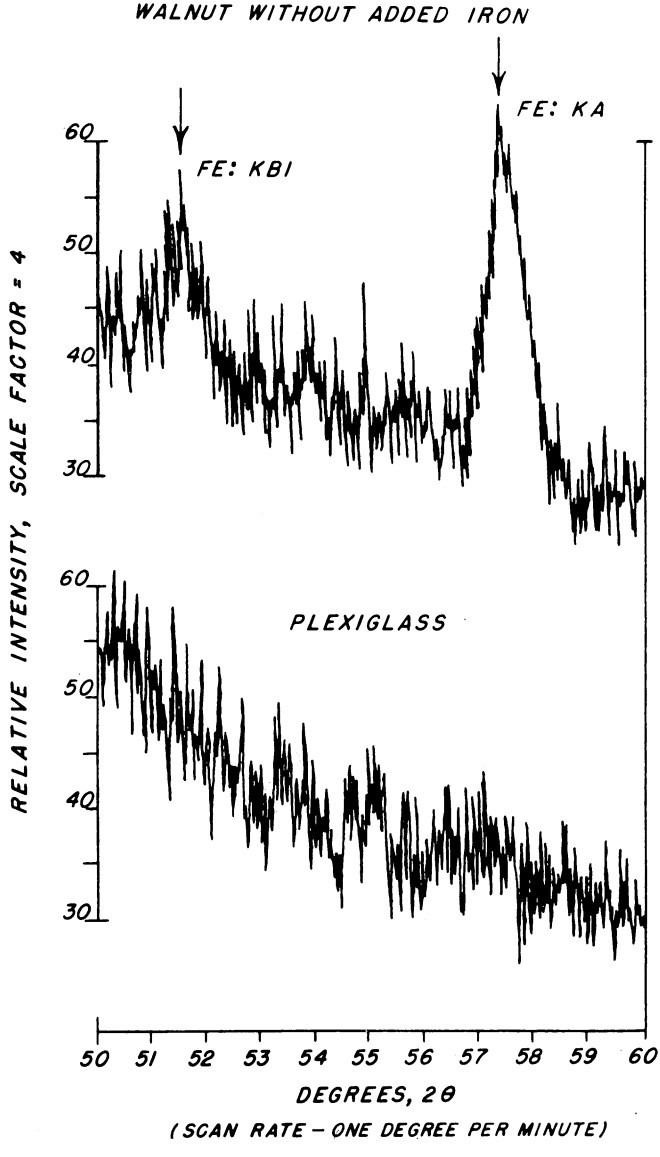

FIG. 10. Iron in walnut or maple.

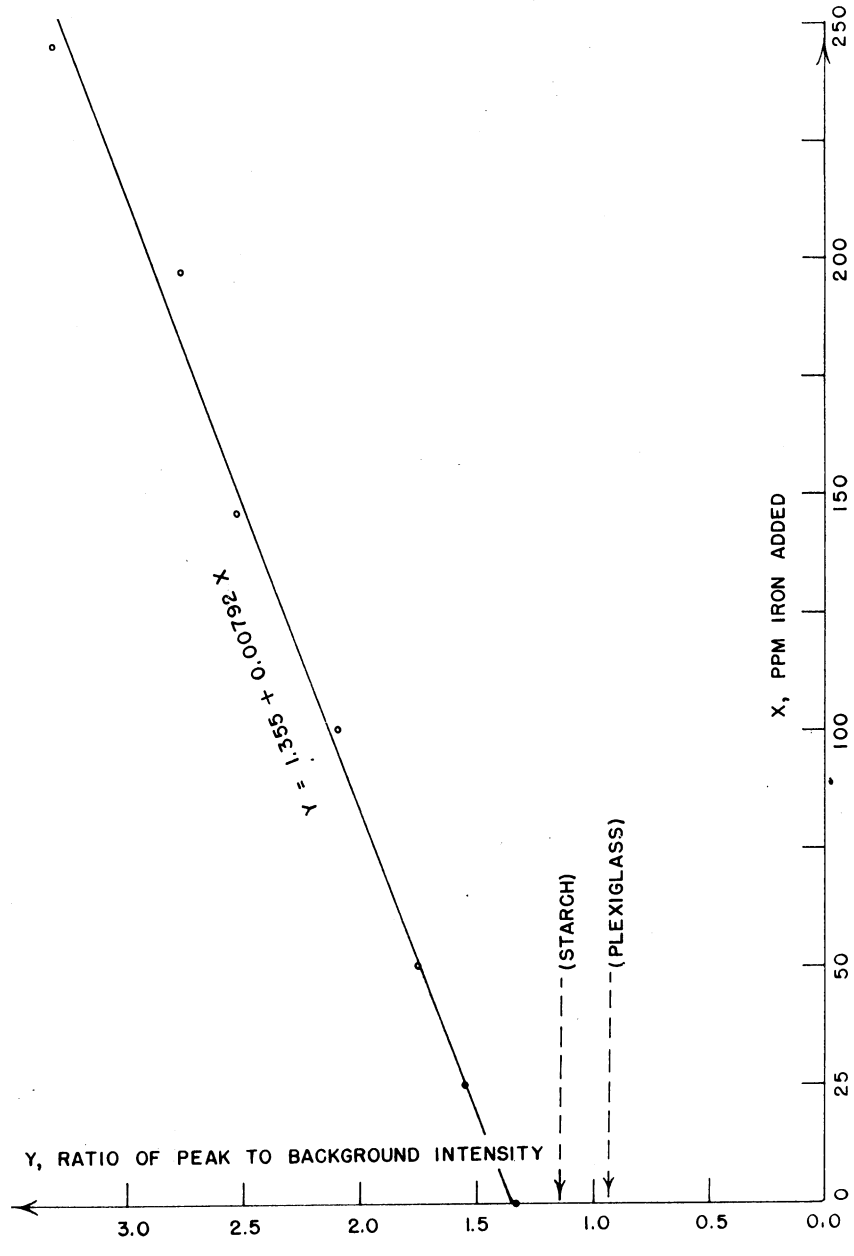

FIG. 11. Calibration curve for iron in walnut or maple.

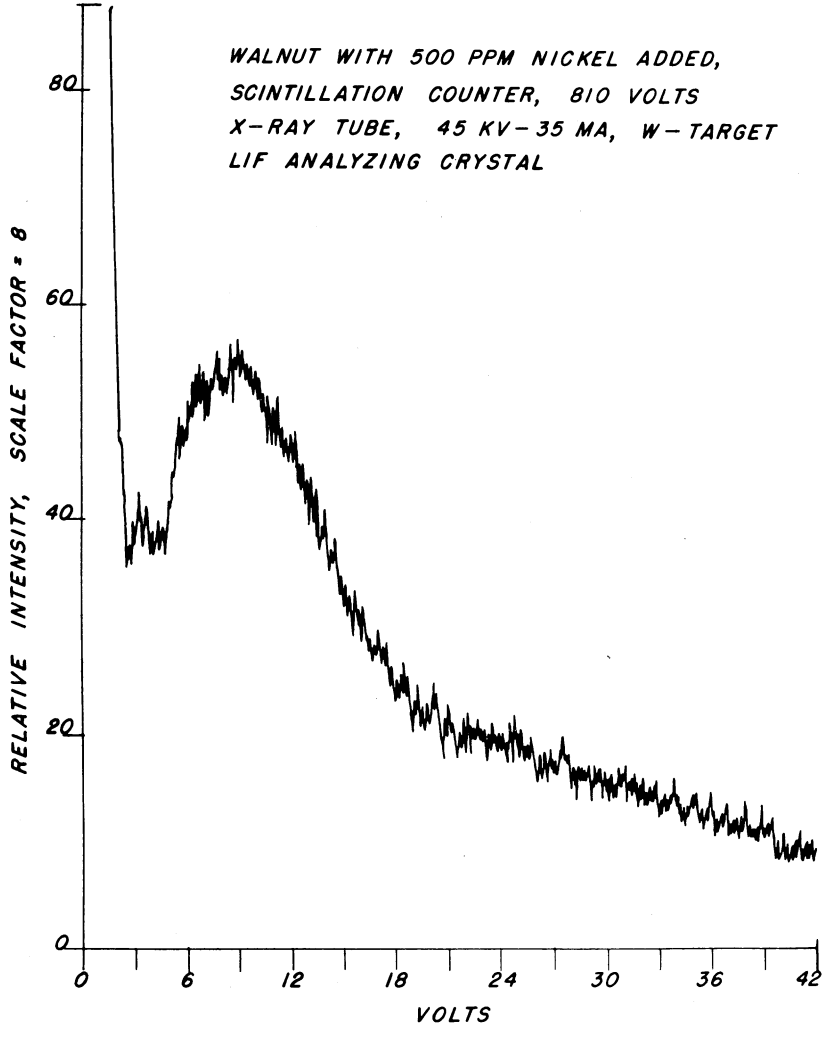

FIG. 12. Pulse height analyzer curve, nickel.

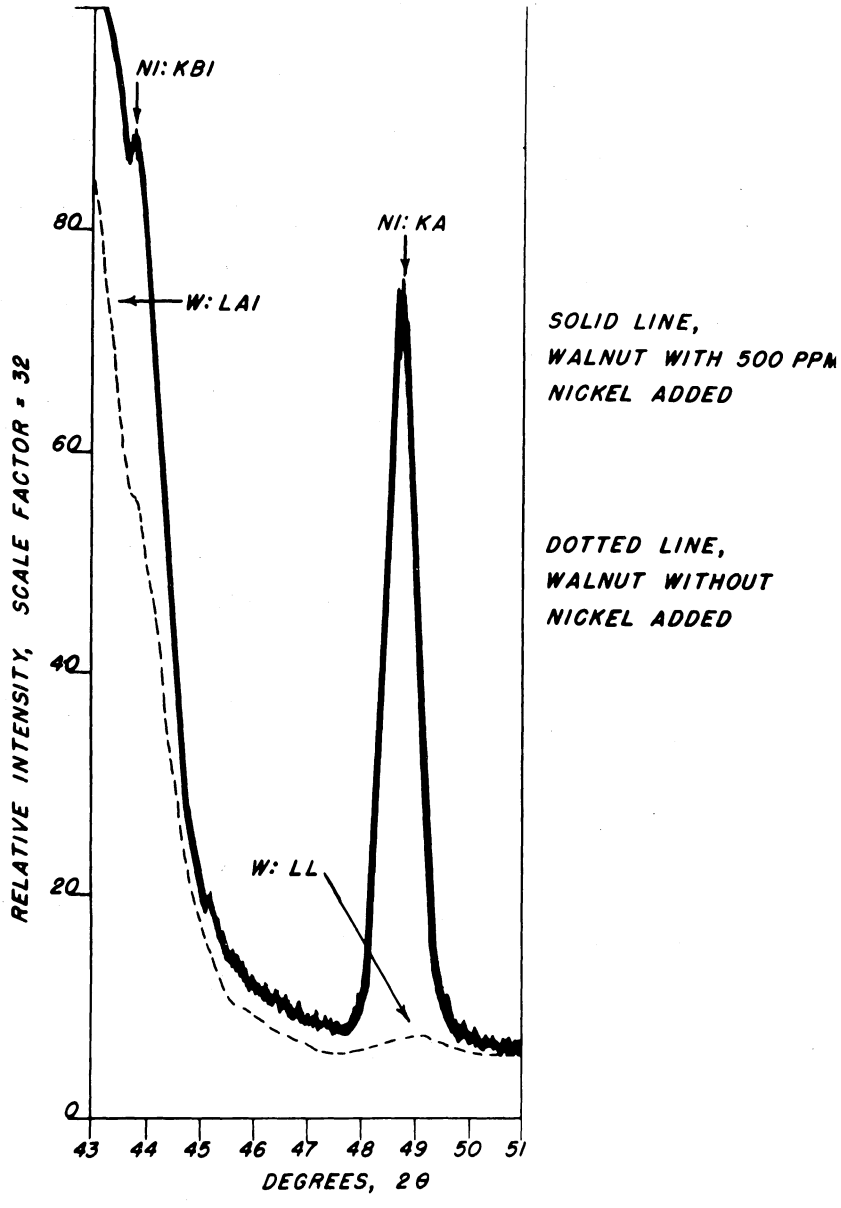

FIG. 13. The nickel region.

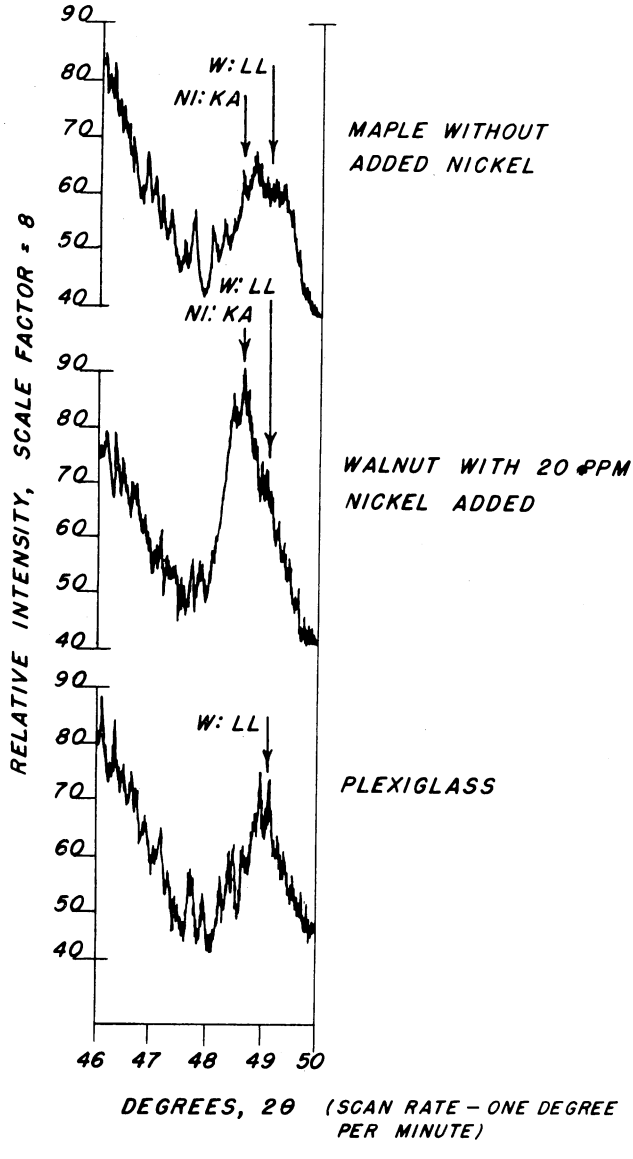

FIG. 14. Nickel in walnut or maple.

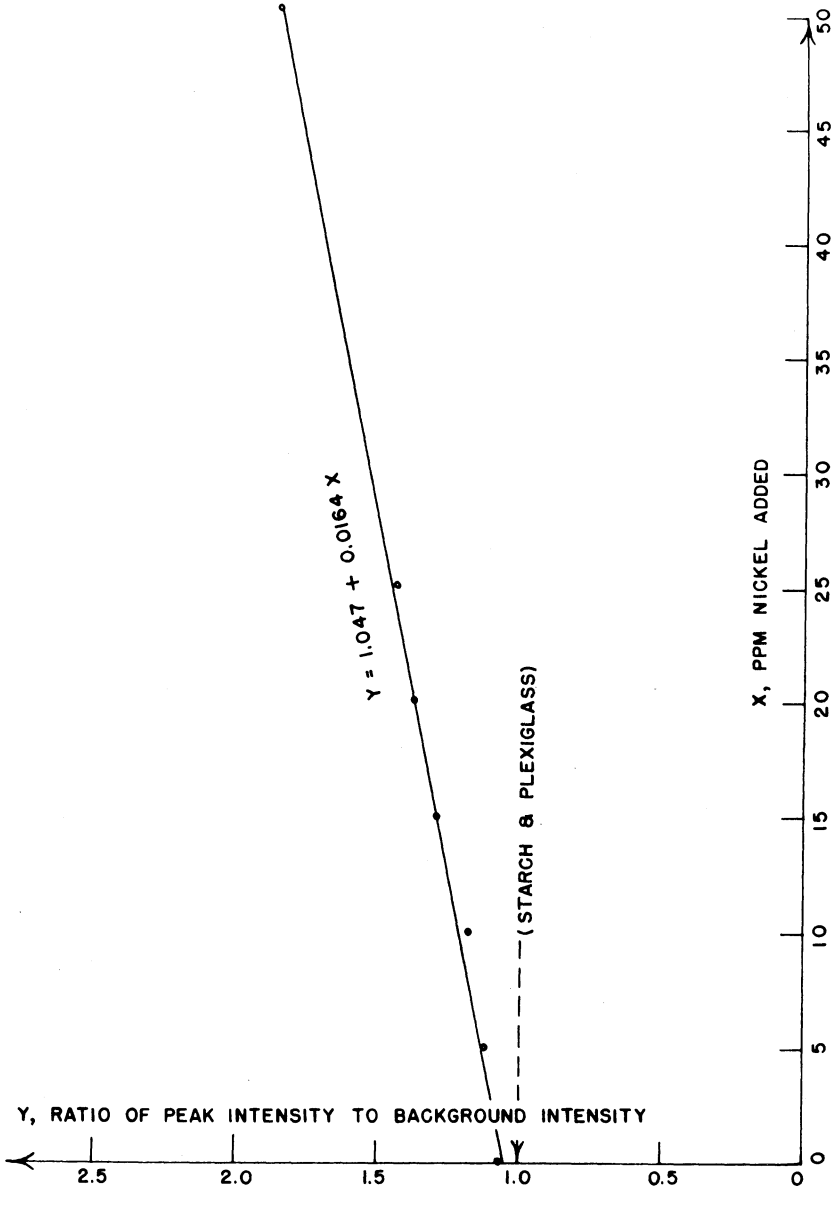

FIG. 15. Calibration curve for nickel in walnut or maple.

The limit of resolution for nickel was 1.9 ppm and the experimental variability was 2.0 ppm for 16,000 counts accumulated. The average amount of nickel was 2.8 ppm in walnut (ranging from 0.0 to 10.4 ppm) and 5.6 ppm in maple (ranging from 0.0 to 14.2 ppm). No values were found in the literature to indicate the amount of nickel expected in wood other than that trace amounts of nickel have been reported (5).

Copper

With copper, PAD curves and calibration curves for both KA and KB lines were considered. This was done to determine which line could be analyzed with the least interference from tungsten peaks in the copper region (Figure 18). Figures 16 and 17 indicate that the KA PAD curve is three to four times the intensity of the KB PAD curve (note the scale factors of 32 and 8, respectively). Figure 18 depicts location and relative intensities of KA and KB lines for copper and tungsten peaks. Intensity of the KB line is about one-half to one-third that of the KA line, which is reflected in the KB PAD curve of Figure 17. More critical scans of Figure 19 show the KA line to be quite strongly obscured by the W:LA1 peak and the KB line bounded on one side by the W:LA1 peak and on the other side by the KA line of zinc present in the wood sample. A comparison of calibration curves of figures 20 and 21 clearly shows the KA line for copper to be a better line for analysis. The KB calibration curve does not have the necessary peak to background ratio for amounts added to provide any advantage over the KA line even when considering great interference from the W:LA1 line. With 25ppm copper added, for example, the KA calibration curve yields a F/S ratio of 1.01; whereas, the KA calibration curve gives a ratio of 1.27 for 25 ppm added. The extent of interference can be demonstrated by a comparison of the KA calibration curve of copper with that of iron, which is a lower atomic number. An F/S ratio for copper of 9.07 was obtained for 1,000 ppm added, which is less than the 9.3 ratio for 1,000 ppm obtained for iron. This is exemplified further by a comparison with the calibration curve for nickel which gave a ratio of 17.45 for 1,000 ppm added (nickel is one atomic number less than copper).

Limit of resolution for the KA line in accumulating 16,000 counts precision was 4.1 ppm; for the KB line, it was 14 ppm. Experimental standard deviation for the KA line was 0.25 ppm and

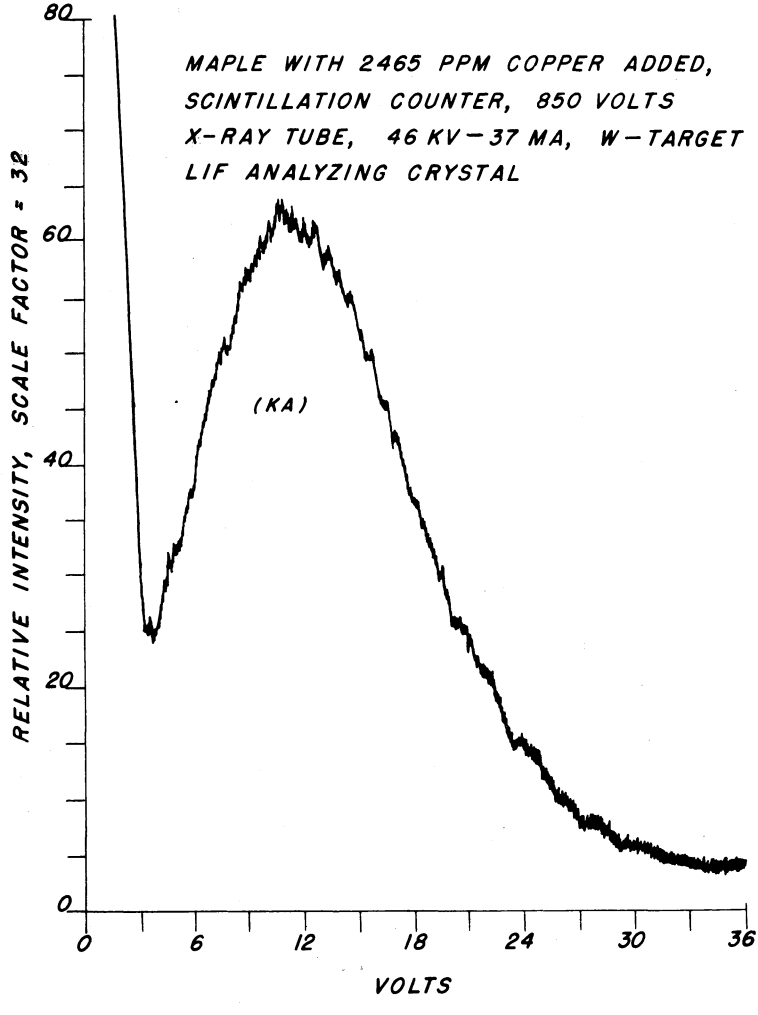

FIG. 16. Pulse height analyzer curve, copper, KA line.

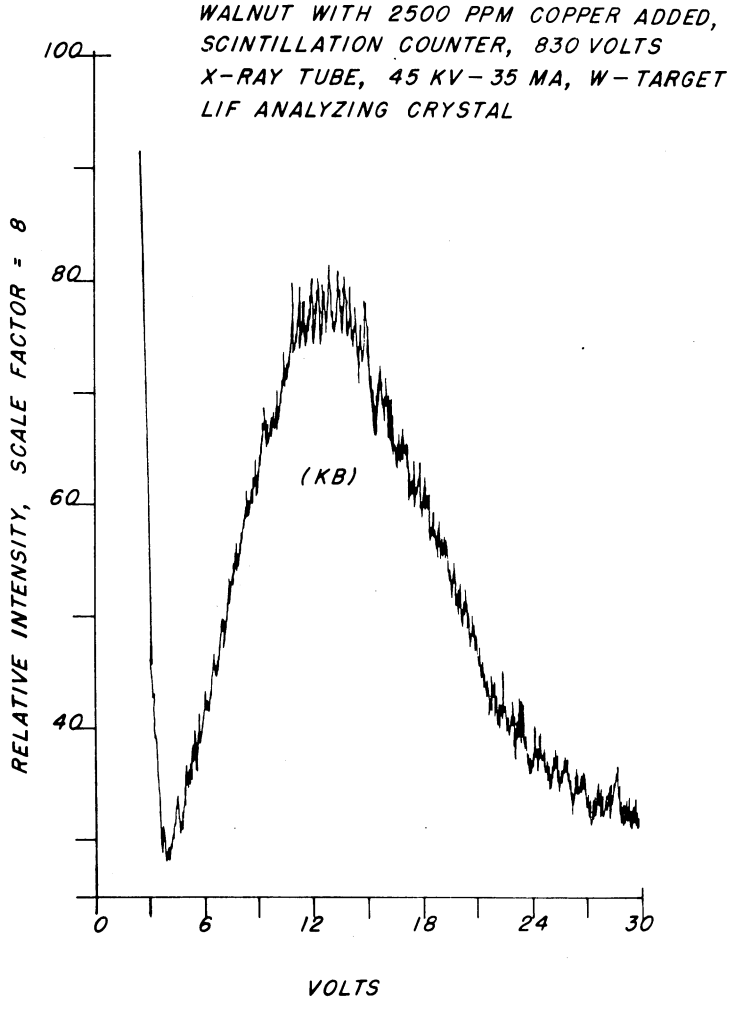

FIG. 17. Pulse height analyzer curve, copper, KB line.

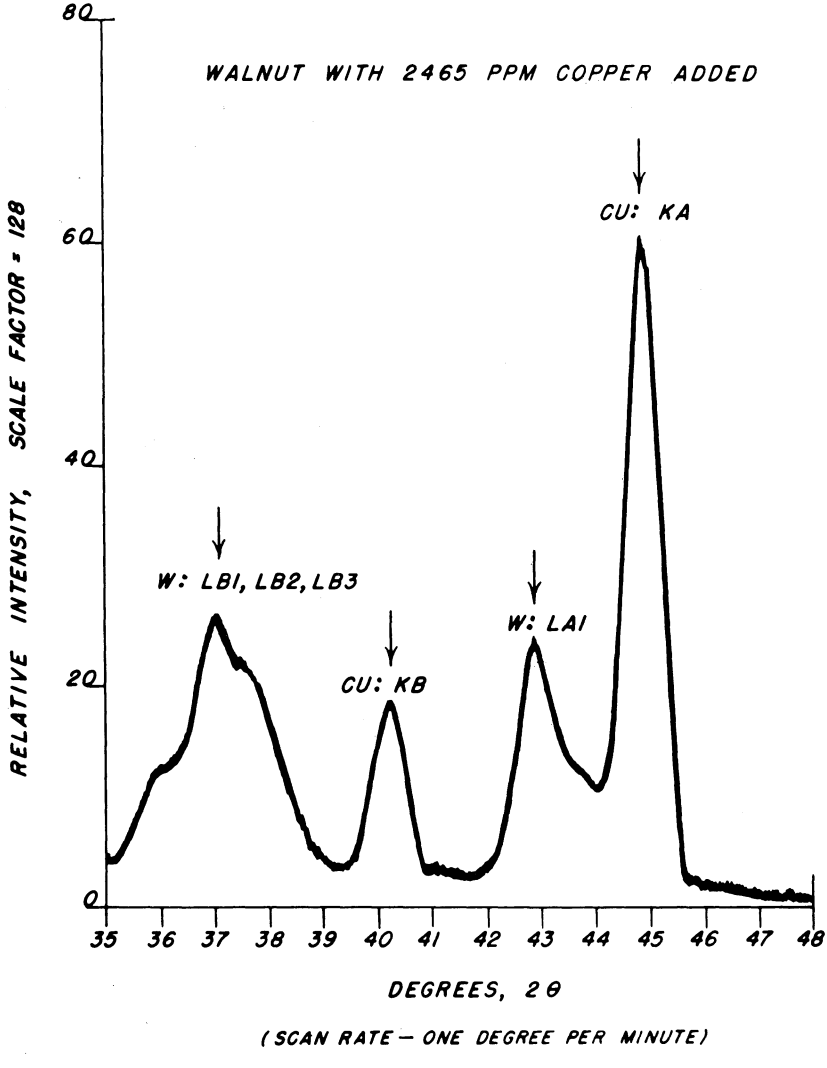

FIG. 18. The copper region.

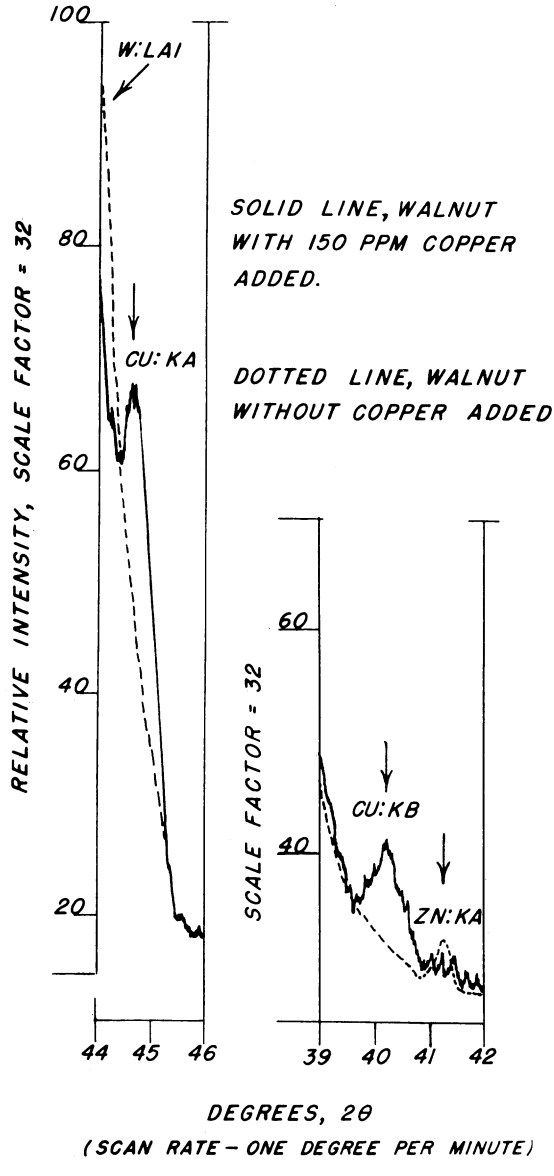

FIG. 19. Copper in walnut or maple.

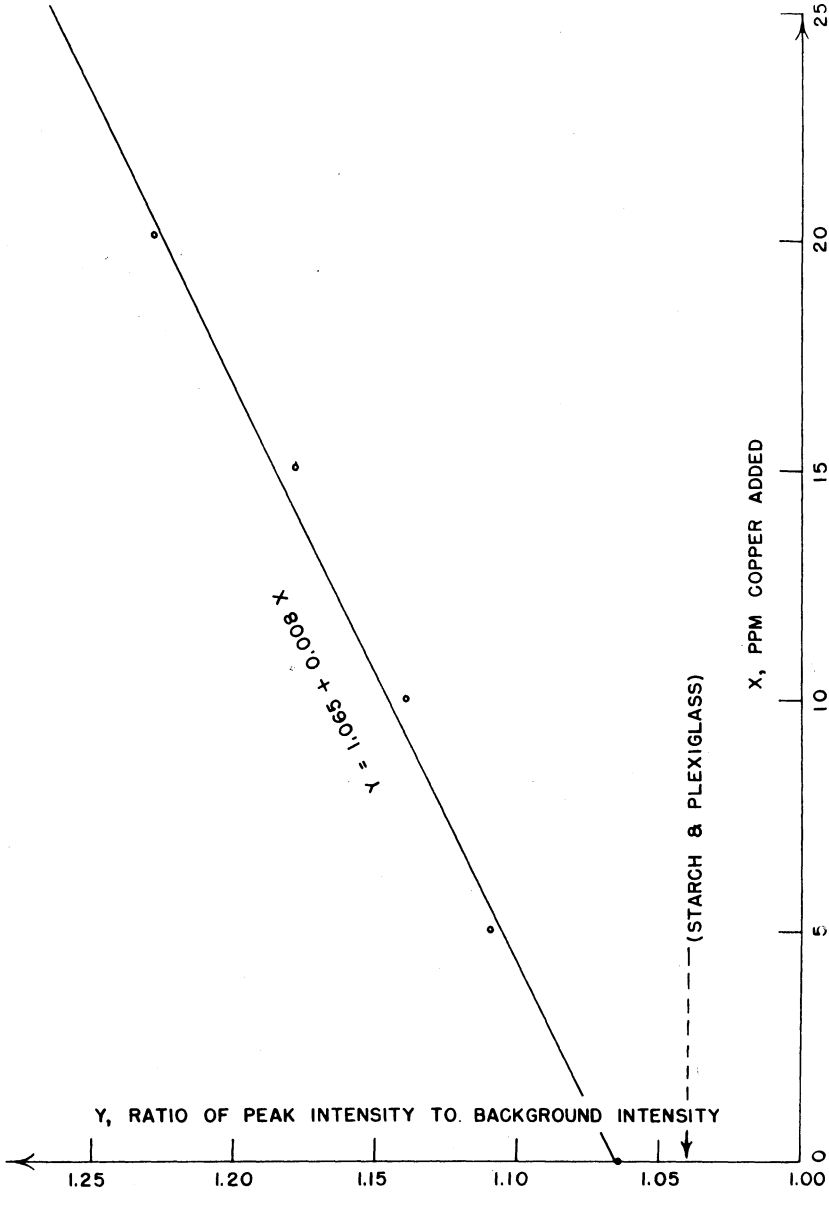

FIG. 20. Calibration curve for copper in walnut or maple, KA line.

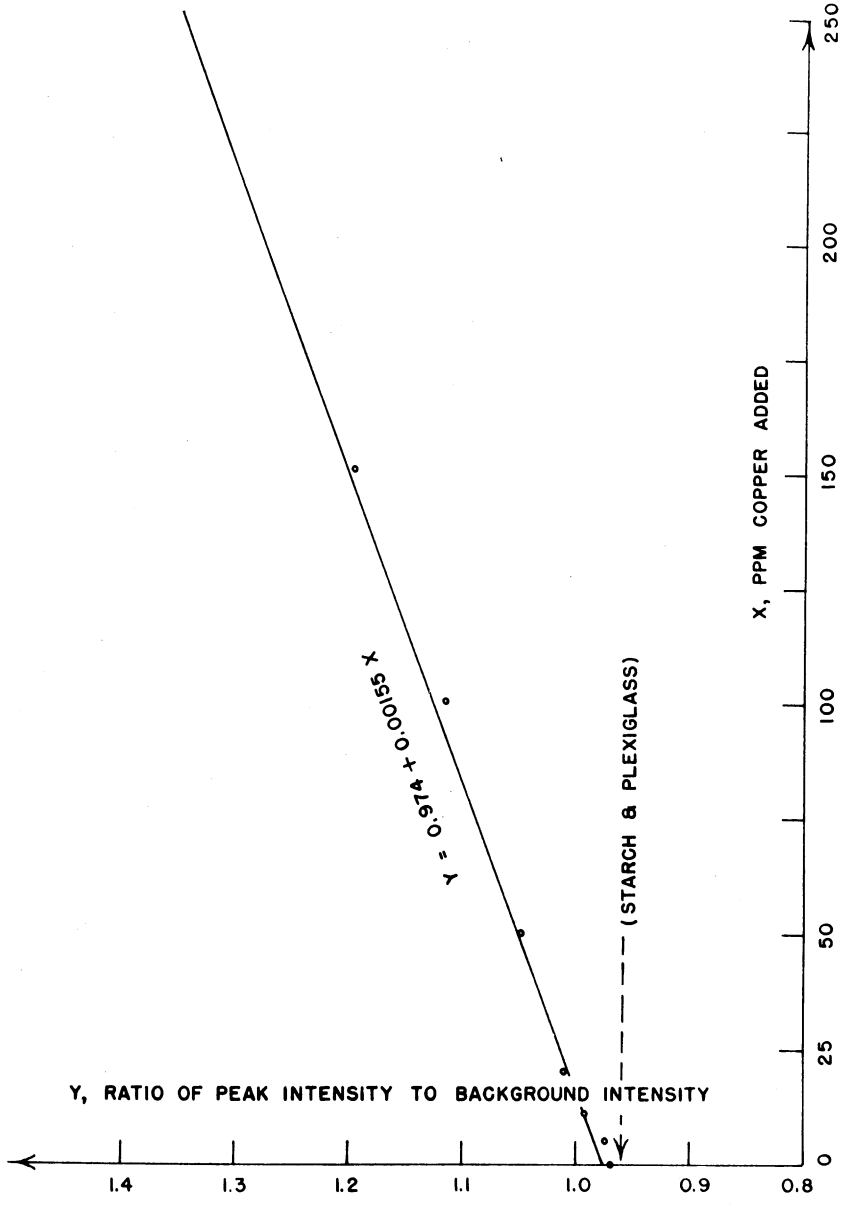

FIG. 21. Calibration curve for copper in walnut or maple, KB line.

1.0 ppm for the KB line. Dixon and Wear *(3)* gave a standard deviation of 2.14 ppm for the KB line of copper using an x-ray spectrograph for analysis of plant tissue (128,000 counts fixed count precision).

Average amount of copper was 6.0 ppm for walnut (ranging from 0.0 to 12.5 ppm) and 6.4 ppm for maple (ranging from 1.2 to 18.7 ppm). Young and Carpenter *(10)* reported a range of 1.0 to 8.0 ppm copper in stems of seedlings and saplings of red maple; Schneider *(8)* gave a range of 1.6 to 4.9 ppm in black walnut. Other workers *(2)* indicated a range of 1.0 to 25 ppm present in plant tissue.

Zinc

PAD curve and analyzing conditions used for zinc are presented in Figure 22. Figure 23 shows the zinc region to be nearly identical to that for the copper KB line with the same tungsten peaks on either side. Critical scans shown in Figure 24 demonstrate that the zinc KA line is located in the trough of two tungsten peaks and is readily detectable for amounts in walnut or maple. The calibration curve for zinc (Figure 25) yields a F/S ratio of 4.23 for 250 ppm added and 13.87 for 1,000 ppm added, which compares favorably to that obtained for nickel (17.45 for 1,000 ppm added). This comparison shows the relative amount of interference from tungsten peaks since zinc is two atomic numbers higher than nickel and can be expected to yield a fluorescent line of greater intensity than nickel for a given amount added.

Limit of resolution for a precision of 32,000 counts was 1.6 ppm and experimental variability was 0.9 ppm in zinc analysis. Whittig *(11)* reported a variability of 1.6 ppm and obtained a slope of calibration of about 0.014 for zinc in plant material. The slope obtained by Whittig approximates that determined in Figure 25 (0.01285).

The average amount of zinc was 12 ppm in walnut (ranging from 3.9 to 65.7 ppm) and 11.7 ppm in maple (ranging from 7.0 to 22.5 ppm). Young and Carpenter *(10)* obtained a range of 2.0 to 62 ppm zinc in stems of seedlings and saplings of red maple; Schneider *(8)* reported a range of 0.0 to 6.6 ppm zinc in black walnut. Other researchers *(2)* found a range of 5.0 to 75 ppm of zinc in plants.

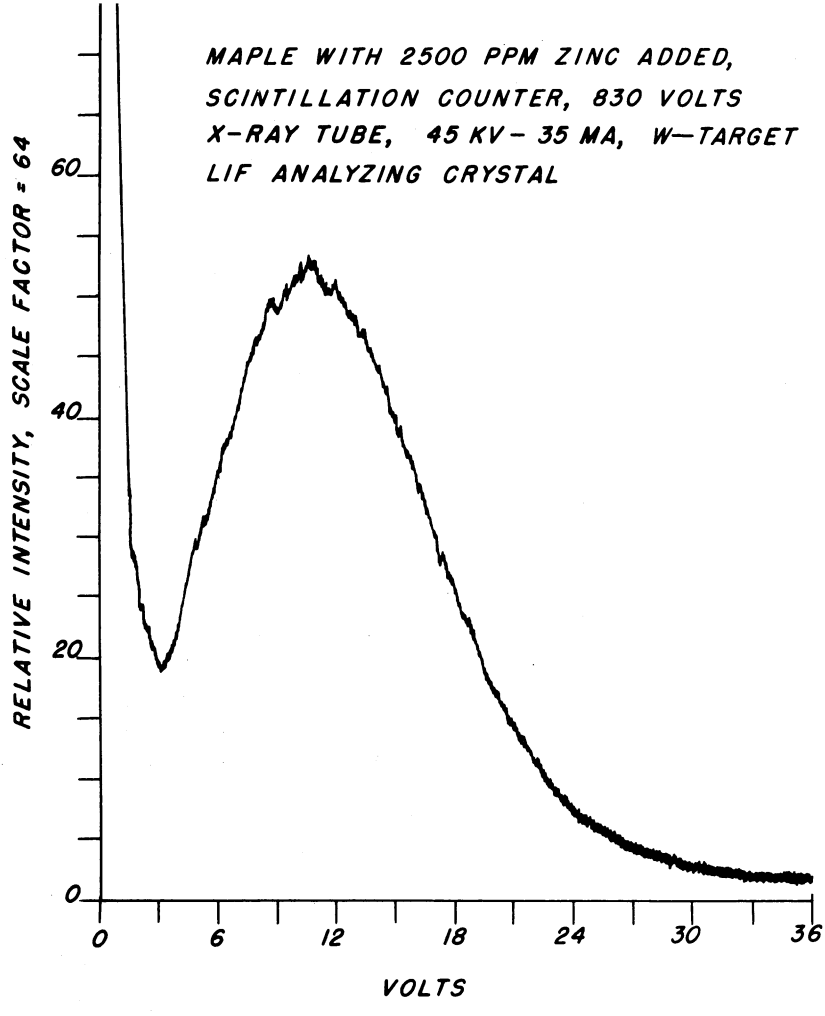

FIG. 22. Pulse height analyzer curve, zinc.

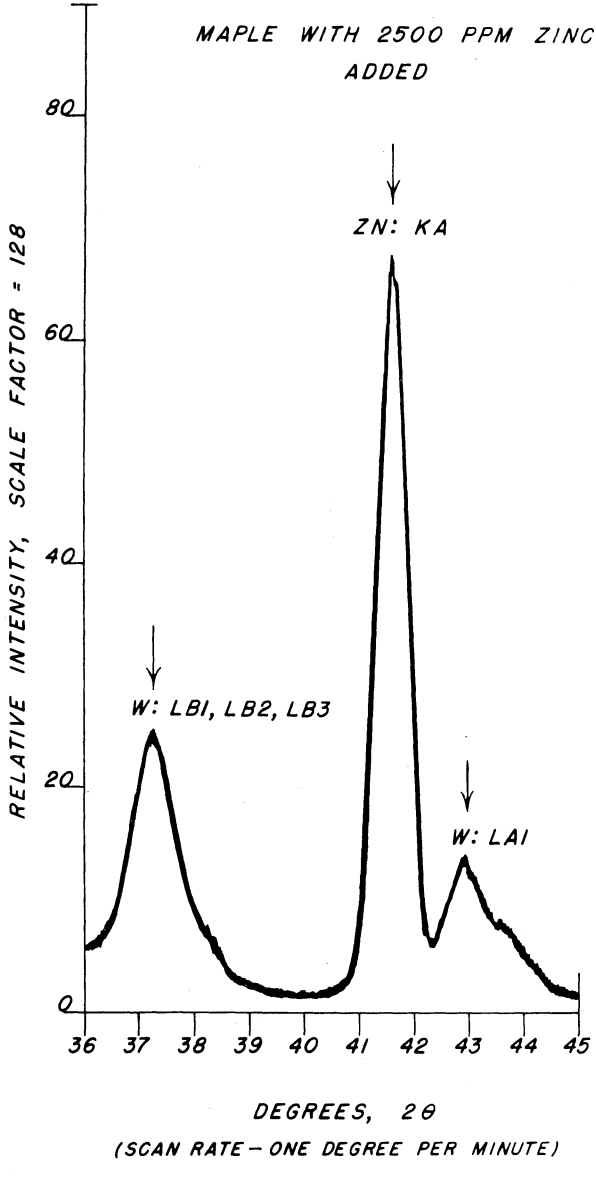

FIG. 23. The zinc region.

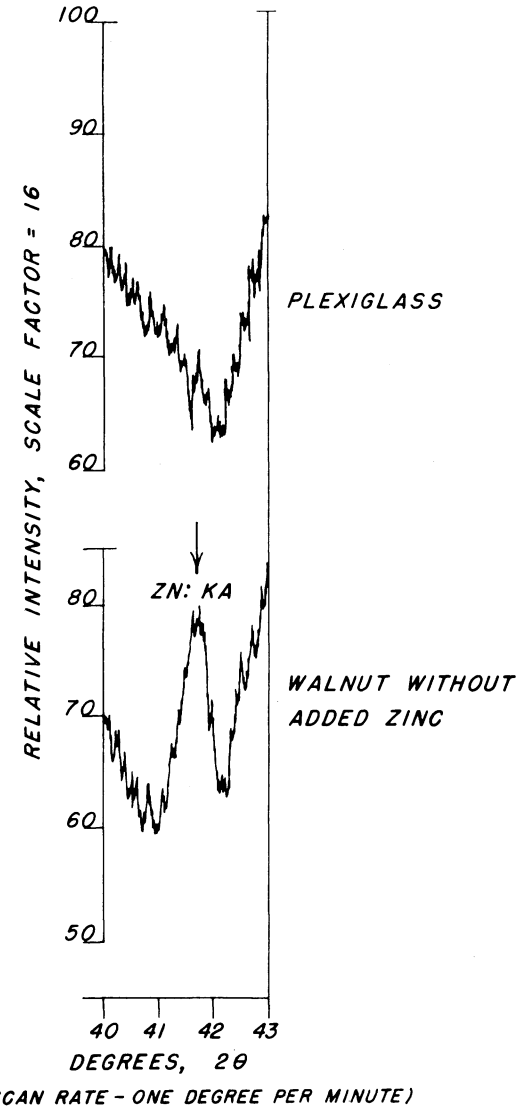

FIG. 24. Zinc in walnut or maple.

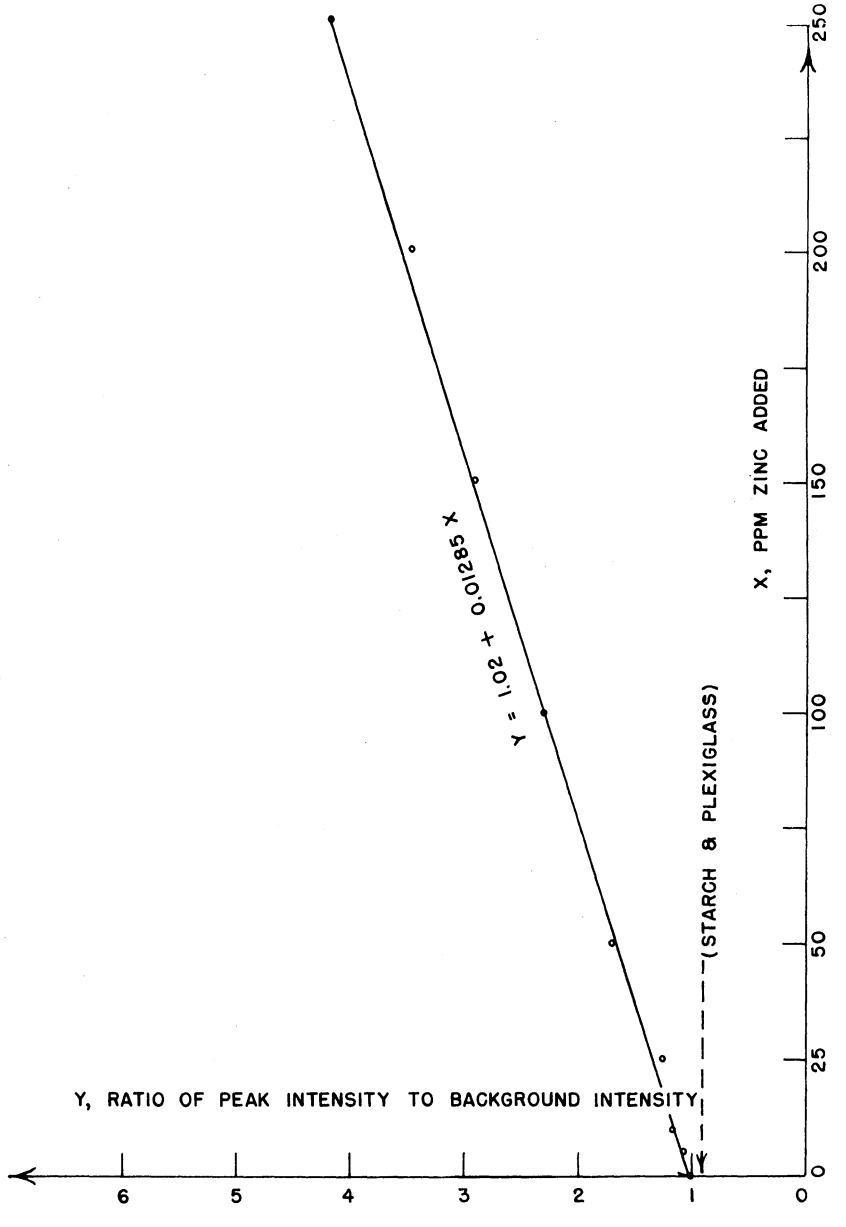

FIG. 25. Calibration curve for zinc in walnut or maple.

SUMMARY AND CONCLUSIONS

Results of this investigation show that utilization of x-ray spectroscopy for elemental analysis of wood provides a degree of success dependent on amounts of specific elements present, their atomic numbers, and the presence of sources of interference (primarily those from the x-ray tube). Claro walnut, black walnut, and bigleaf maple all produced the same slopes of calibration regardless of element analyzed. This similarity in calibration is a result of similar matrices of these species and similar amounts present of elements analyzed. Claro walnut and black walnut were considered a single species in this study.

Of 23 elements reported in wood, 11 were detectable (aluminum, silicon, phosphorus, chlorine, potassium, calcium, manganese, iron, nickel, copper, and zinc). Aluminum, phosphorus, and manganese were present in amounts yielding such low intensities of flourescence that resolution times for precision of measurement were prohibitive. As a result, these three elements were calibrated, but only a few randomly selected samples of walnut and maple were analyzed for averaging purposes.

Silicon and chlorine were detected but were not calibrated since neither yielded suitable calibration curves (interference from undetermined sources). Therefore, no attempt was made to determine average amounts of chlorine and silicon.

Only potassium, calcium, iron, nickel, copper, and zinc met all requirements of detectability and were analyzed fully. Potassium, calcium, iron, and zinc were quantitatively detectable with excellent results; nickel and copper were detectable with somewhat less success caused by trace amounts present and strong interference from tungsten lines of the x-ray tube. Despite strong interference from the W:LA1 line for the KA line of copper, the KA line yielded better resolution than the second order KB line. With nickel, the W:LL line was the limiting interference in resolution (tables 4 and 5 indicate resolution limits and experimental variability determined for K, Ca, Fe, Ni, Cu, and Zn; Table 6 provides average and range of amounts detected). There is considerable heterogeneity for potassium and calcium within both walnut and maple as indicated by a comparison of resolution limits with much larger experimental standard deviations (Table 4).

Resolution limits, for the 95 percent confidence level and the analysis techniques employed, were estimated to be as follows:

TABLE 4. CONFIDENCE LEVELS FOR LIMITS OF RESOLUTION AND EXPERIMENTAL VARIABILITY OF EACH ELEMENT CALIBRATED USING THE PROPORTIONAL COUNTER

Wood	Element	Line	Accumulated counts	Sigma level %	Resolution limit (ppm)	Standard deviation (ppm)
Walnut	K	KA	16,000—P*	99	1.3	169.2
			2,000—B**	95	0.9	112.8
				67	0.4	56.4
Maple	K	KA	16,000—P	99	1.3	108.0
			2,000—B	95	0.9	72.0
				67	0.4	36.0
Walnut	Ca	KA	64,000—P	99	0.3	294.6
			400—B	95	0.2	196.4
				67	0.1	98.2
Maple	Ca	KA	64,000—P	99	0.3	133.8
			400—B	95	0.2	89.2
				67	0.1	44.6

* P= peak ** B = background.

TABLE 5. CONFIDENCE LEVELS FOR LIMITS OF RESOLUTION AND EXPERIMENTAL VARIABILITY OF EACH ELEMENT CALIBRATED USING THE SCINTILLATION COUNTER

Wood	Element	Line	Accumulated counts	Sigma level %	Resolution Limit (ppm)	Standard deviation (ppm)
Walnut & maple	Fe	KA	16,000—P*	99	5.6	6.7
			16,000—B**	95	3.7	4.5
				67	1.9	2.2
Walnut & maple	Ni	KA	16,000—P	99	2.9	6.1
			16,000—B	95	1.9	4.0
				67	1.0	2.0
Walnut & maple	Cu	KA	16,000—P	99	6.2	0.8
			16,000—B	95	4.1	0.5
				67	2.1	0.25
Walnut & maple	Cu	KB	16,000—P	99	21.0	2.8
			16,000—B	95	14.0	1.9
				67	7.0	1.0
Walnut & maple	Zn	KA	32,000—P	99	2.4	2.7
			32,000—B	95	1.6	1.8
				67	0.8	0.9

* P= peak ** B = background.

46.4 ppm for Al, 33 ppm for P, 0.9 ppm for K, 0.2 ppm for Ca, 18.5 ppm for Mn, 3.7 ppm for Fe, 1.9 ppm for Ni, 4.1 ppm for Cu, and 1.6 ppm for Zn. Resolution limits assume homogeneity; for K and Ca, there appears to be a large amount of heterogeneity within woods utilized for calibration purposes. The amount of heterogeneity is indicated by experimental variabilities obtained (36 to 56.4 ppm for K and 44.6 to 98.2 ppm for Ca). Wood of walnut had higher values.

For elements fully analyzed (potassium, calcium, iron, nickel, and zinc), higher concentrations were present in figured wood

TABLE 6. AVERAGE AND RANGE OF AMOUNTS IN ppm OF THE SIX ELEMENTS ANALYZED AS DETERMINED IN THE WALNUTS AND IN MAPLE FOR FIGURED PLUS UNFIGURED SPECIMENS

Element		*Juglans nigra* L. and *J. hindsii* Jeps	*Acer macrophyllum* Pursh
		(ppm)	
Potassium	Average	545	763
	Range	180-1,050	350- 1,850
Calcium	Average	1957	2,118
	Range	950-6,080	1,250-11,420
Iron	Average	93.2	70.8
	Range	20-198	12-141
Nickel	Average	2.8	5.6
	Range	0-10.4	0-14.2
Copper	Average	6.0	6.4
	Range	0-12.5	1.2-18.7
Zinc	Average	12.0	11.7
	Range	3.9-65.7	7.0-22.5

than in unfigured wood (in both walnut and maple). Although concentrations were higher in figured wood, statistical analysis indicated that only higher concentrations of iron in figured maple samples were consistently significantly different from unfigured samples at the 95 percent level and higher when compared by element and within sequential series of 1-inch cubical samples radially from the pith outward. There was no pattern found in concentrations of any element or elements in walnut and maple samples analyzed with respect to distance from the pith. Statistically, comparison of individuals (cross sections) within a species (walnut or maple) showed that amounts of each of the six elements differ significantly between individuals at the 97.5 percent level and greater; within individuals, however, only potassium and iron in the walnuts, and potassium and zinc in maple differed significantly at the 89 percent level and higher.

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