Standard Copper Wave-Lengths in the Region 100A to 450A

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The copper spectrum has been photographed in the region 100A to 450A with a twenty-one foot grazing incidence vacuum spectrograph. The wave-length of sharp copper lines (approximately two every Angstrom) have been determined by interpolating between known aluminum and oxygen lines with the formula $\lambda=\lambda_0+Ax+Bx^2+Cx^3\cdots$. A discussion of the errors in the wave-lengths is given.

I. INTRODUCTION

PREVIOUSLY available standard wave-lengths in the region 100–450A consisted of aluminum lines which had been measured by Söderqvist and Edlén.[1] In addition, the authors had an unpublished list of oxygen standards due to B. Edlén. However, there were not a sufficient number of these standards for convenient interpolation when using an instrument of high dispersion. Thus, in order to bridge the gaps in the above lists, the secondary standards listed in Table II were established.

The copper spectrum was chosen because it has a large number of strong, sharp lines well distributed throughout the region. Moreover, the copper spectrum is more easily excited than either oxygen or aluminum.

II. EXPERIMENTAL

The instrument[2] used was a 21-foot grazing incidence vacuum spectrograph which was constructed by the Mann Instrument Company of Cambridge, Massachusetts, and which has dispersions given in Table I. The grating was ruled on glass 30,000 lines per inch by R. W. Wood and H. M. O'Bryan at The Johns Hopkins University.

TABLE I. *Dispersion: Angle of incidence 87°.*

100A	0.215 A/mm
200A	.295
300A	.356
450A	.432

The electrodes were made of copper, size 1 inch by 1/4 inch diameter, thin copper shells cored with aluminum, and a copper shell packed with an oxide of boron. The latter was used as the lower (positive) electrode with an upper (negative) electrode of solid copper in obtaining the oxygen spectrum. The copper shells on the aluminum electrodes tended to prevent uneven wearing away of the aluminum, and also served to indicate any relative shift of the lines of adjacent aluminum (oxygen) and copper spectra. The vacuum spark was less than a millimeter in length when operated in a vacuum of 10^{-5} mm of Hg or better at a d.c. potential of 100 kv.

III. CALCULATION

Interpolations between the above-mentioned standard oxygen and aluminum lines were made by use of the relation,

$$\lambda=\lambda_0+Ax+Bx^2+Cx^3+\cdots, \qquad (1)$$

where λ_0 is a known standard, x is the distance along the plate from λ_0 to λ (i.e., the difference of the two comparator readings, and hence either positive or negative), and A, B, C are constants.

This relation is derived from the grating equation (where ϕ is the angle of diffraction) by expressing $\sin\phi$ in terms of the radius, R, of the Rowland circle, and the length of arc, X, from the center of the grating to λ_0, plus (or minus) an increment of arc, x, from λ_0 to λ, thus

$$\lambda=e\sin\theta-e\sin\phi$$
$$=e\sin\theta-e\cos[(X+x)/2R]. \qquad (2)$$

[1] Söderqvist and Edlén, Zeits. f. Physik **69**, 356 (1931).
[2] P. G. Kruger, Rev. Sci. Inst. **4**, 128 (1933).

The last term may be expanded in terms of two angles, one constant and the other variable. By further expanding cos $(x/2R)$ and sin $(x/2R)$ as power series, and collecting terms in powers of x, the following equation is obtained.

$$\lambda = e\left(\sin\theta - \cos\frac{X}{2R}\right) + \left(\frac{e}{2R}\sin\frac{X}{2R}\right)x + \left(\frac{e}{8R^2}\cos\frac{X}{2R}\right)x^2 + \left(-\frac{e}{48R^3}\sin\frac{X}{2R}\right)x^3 + \cdots, \quad (3)$$

whence, comparing Eq. (1),

$$C = -A/24R^2. \quad (4)$$

The constants A and B for any region are calculated from λ_0 and two other known standards λ_1 and λ_2 lying 6–10 cm distant from, and on opposite sides of, λ_0. This is done by solving the simultaneous equations,

$$\begin{aligned} \lambda_1 - \lambda_0 &= Ax_1 + Bx_1^2, \\ \lambda_2 - \lambda_0 &= Ax_2 + Bx_2^2, \end{aligned} \quad (5)$$

for A and B. For values of x less than 10 cm the value of the term Cx^3 is less than 0.001A.

For larger values of x the cubic term is used. In this case Eqs. (5) become cubic equations, but they may be reduced to equations with one less constant by the use of Eq. (4), and solved as before. That is, Eqs. (5) become

$$\begin{aligned} \lambda_1 - \lambda_0 &= A(x_1 - x_1^3/24R^2) + Bx_1^2, \\ \lambda_2 - \lambda_0 &= A(x_2 - x_2^3/24R^2) + Bx_2^2. \end{aligned} \quad (6)$$

C is then found from Eq. (4) by using the measured value of R which is sufficiently accurate. In dividing the spectrum into these regions, care was taken that a known standard occurred near the middle of the region (λ_0), and that the remainder of the standards were as advantageously distributed as possible for drawing a correction curve.

IV. Discussion

The wave-lengths of the lines were determined by making measurements on three different plates. Four readings were taken per line on each of the three plates so that a total of twelve settings were made on each line.

From these data, the wave-lengths were calculated in the manner outlined in Part III, each separate calculation covering a range of 30–60A. Correction curves were then drawn using all the available primary standards in the region, and the corrections so determined were applied to the calculated wave-lengths. These corrections served to compensate for minor deviations from the formula, and also to smooth out small irregularities within the primary standards. The maximum corrections rarely exceeded 0.07A and were usually much smaller. In selecting the regions for calculation, care was taken to see that the regions from different plates overlapped. Consequently maximum corrections on one set of data coincided with small corrections on another.

The number of standards available for drawing these correction curves was adequate except at long wave-lengths (350–470A). Here there were a few regions where the oxygen standards were so widely spaced that the correction curves may be open to some question. In the region 400–435A, second order copper lines were used to supplement the oxygen lines.

While making the measurements it was noticed that there was a slight shift between the oxygen and copper spectra. This was observable due to the appearance, in the oxygen spectrum, of copper lines from the copper shell of the electrodes, and was probably caused by a temperature change between exposures, though the temperature was kept constant to about ± 0.04°C during a set of exposures.

This shift was measured and found to be positive (add $\Delta\lambda$ shift to correct λ) on one plate, negative by the same amount on the second and negative by a slightly larger amount on the third plate. Since the shift in $\Delta\lambda$ was practically constant for a plate this error was easily corrected by adding or subtracting the proper amount when the averages were taken. Further, the three sets of data were given different weights in various wave-length regions, the weights being determined from the size of the correction curve and its smoothness.

In Table III there are listed various wave-

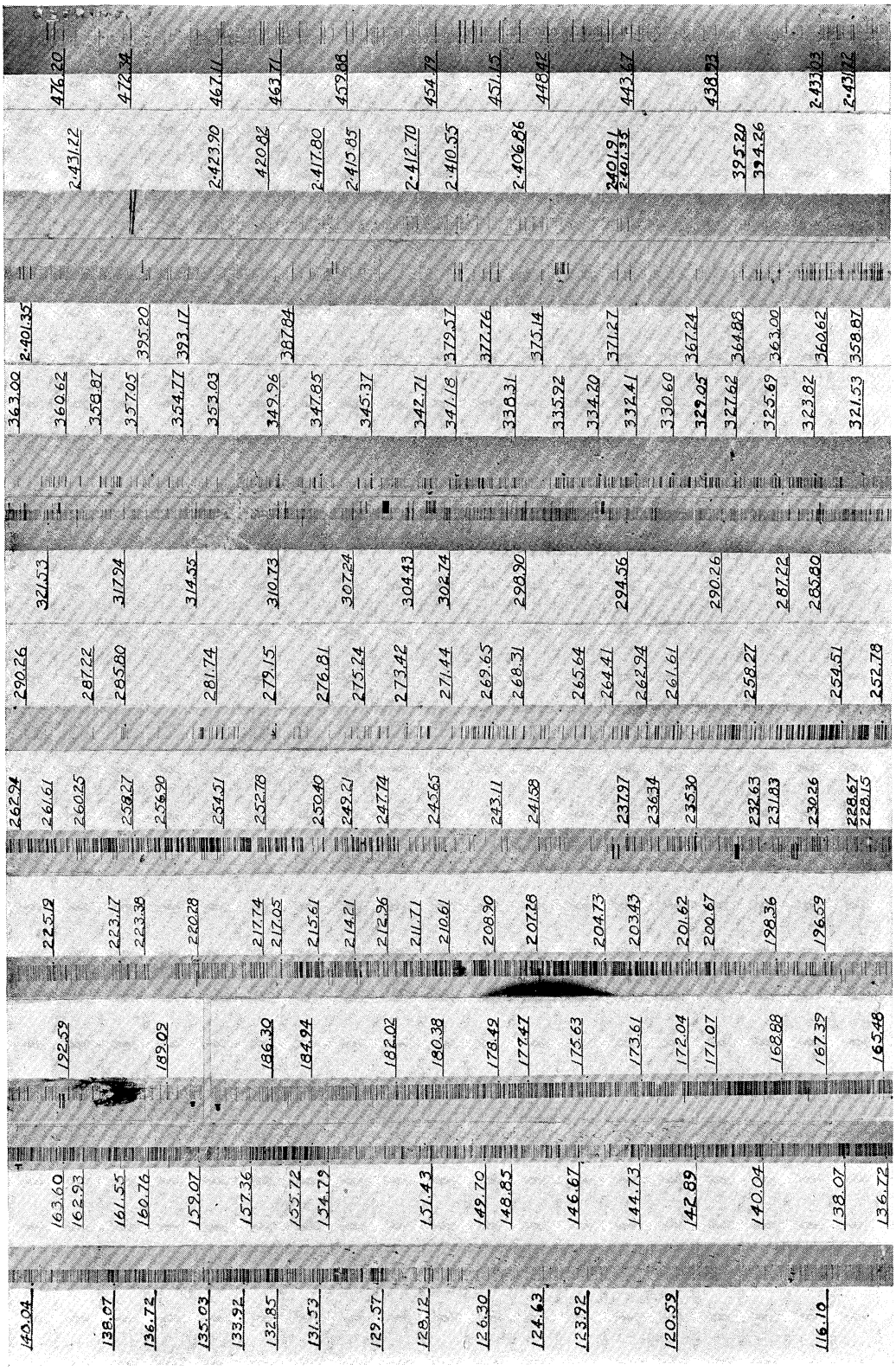

FIG. 1. The copper spectrum with standard lines indicated. Overlapping spectra are due to oxygen, aluminum, and boron.

TABLE II. *Standard wave-lengths of copper lines.*

Int.	λ (vac.)	Int.	λ (vac.)	Int.	λ (vac.)	Int.	λ (vac.)	Int.	λ (vac.)	Int.	λ (vac.)	Int.	λ (vac.)
	A		A		A		A		A		A		A
10	109.123	40	155.136	9	194.357	2	237.406	10	274.269	10	332.405*	4	2–407.148
12	109.215	15	155.718	10	196.363	10	237.969	15	274.601	100	332.893	5	2–407.623*
7	109.818	20	156.153	30	196.585	15	241.583	10	275.244	30	333.562	5	2–407.677*
7	110.637	20	156.557	30	197.128	4	242.882	10	275.829	30	334.204	7	2–409.443*
10	110.741	20	156.847	30	197.598	4	243.108	10	276.805	20	335.016	10	2–410.548
10	111.756	40	157.359	5	198.364	1	244.411	10	277.761	15	335.470	10	2–411.093
12	112.532	15	158.080	7	198.850	2	245.418	20	278.128	25	335.919	8	2–411.210
6	113.120	20	158.702	10	199.723	2	245.653	10	279.150	25	336.279	15	2–412.702
8	113.928	10	159.072	7	200.417	1	246.286	8	280.802	8	336.577*	10	2–413.234
7	114.033	10	159.462	100	200.674	2	246.852	50	281.492	25	338.314	5	2–413.681*
7	115.143	4	159.919	75	200.860	10	247.336	40	281.744	10	339.038*	3	2–413.813*
8	115.766	15	160.530	50	200.958	25	247.742	20	282.440	15	339.420	3	2–414.558*
10	116.099	50	160.763	15	201.329	10	248.153	6	285.798	30	339.887	3	2–415.853*
7	116.229	30	161.551	20	201.615	50	248.426	10	285.873	20	341.183	10	2–417.799
7	117.079	25	161.748	20	202.065	7	248.858	8	287.215	25	341.483	10	2–418.949
15	120.594	20	162.078	60	203.010	20	249.213	0	289.358*	20	342.432*	5	2–419.292*
9	123.286	10	162.651	60	203.432	15	249.415	0	290.259*	80	342.713	5	419.355*
20	124.630	20	162.926	15	204.056	10	249.908	2	291.800*	5	343.059*	5	420.820*
20	126.298	30	163.271	40	204.725	30	250.400	10	293.257*	8	344.075*	3	2–421.876*
20	127.105	25	163.598	60	205.278	4	250.816	3	293.409*	5	344.179*	8	2–422.213*
25	127.444	20	164.259	30	205.610	20	251.278	0	294.094*	8	344.866*	5	2–422.310*
25	128.012	15	164.675	10	205.984	20	251.670	5	294.561*	90	345.368	2	2–423.400*
25	128.123	30	165.127	60	206.355	20	251.947	5	295.350*	60	346.004	3	426.668*
30	128.255	25	165.481	35	206.842	15	252.223	1	295.516*	30	347.854	0	2–428.414*
15	128.523	8	166.023	20	207.282	75	252.780	10	297.057*	15	348.413	10	2–431.215
10	129.398	12	166.308	15	207.733	15	253.083	10	297.647*	30	349.964	1	2–431.349*
40	129.567	10	166.645	35	207.925	15	253.465	5	298.017*	10	350.056	1	2–431.995*
20	129.697	5	166.958	15	208.502	15	253.786	20	298.901*	8	350.421	9	2–432.120*
10	129.890	10	167.392	60	208.902	50	254.510	15	299.217	5	350.824	0	2–432.502*
15	130.438	15	168.111	30	209.241	70	254.772	5	300.074	5	351.538	7	2–432.626*
18	130.671	15	168.423	30	209.648	45	255.214	1	300.823*	15	353.031	4	2–432.899*
20	130.739	30	168.881	15	210.217	35	255.417	1	301.437*	10	353.568	2	2–433.034*
15	131.015	15	169.488	15	210.612	30	256.365	5	302.000*	8	354.771	1	438.929*
15	131.533	15	169.765	50	211.109	40	256.898	8	302.735*	20	355.425	5	443.233
35	131.590	15	170.007	20	211.707	20	257.315	10	304.434	5	355.977*	10	443.666
7	132.149	15	170.645	10	212.339	20	257.626	8	304.656	3	356.643*	3	444.214*
12	132.528	15	171.074	10	212.964	15	258.004	4	307.238	10	357.052	15	444.999*
50	132.848	20	171.215	8	213.617	45	258.265	20	310.380	100	357.897	2	445.391*
40	133.389	40	172.036	20	214.206	4	258.609	15	310.727	90	358.865	10	446.359
40	133.916	5	172.810	10	214.460	80	258.927	20	312.505	50	359.873	25	446.995
60	134.550	10	173.193	10	214.861	20	259.199	9	312.833	30	360.618	25	448.420
20	135.025	5	173.605	50	215.611	20	259.558	2	313.890*	25	361.220	25	450.015
30	135.846	10	173.990	50	216.063	25	259.871	6	314.545	15	361.838	25	451.152
45	136.724	9	174.507	25	216.454	25	260.245	6	315.873*	8	363.003	5	452.223*
40	136.936	8	174.885	8	217.052	25	260.967	4	316.873*	10	363.967	4	452.500*
75	138.074	30	175.484	20	217.743	30	261.606	7	317.937	5	364.876	30	452.654
50	138.115	25	175.633	4	219.227	20	261.806	2	318.763*	9	364.870	20	453.130*
50	140.042	15	176.232	6	219.927	20	262.442	2	319.845*	3	367.238*	40	453.425
30	141.694	10	176.824	6	220.277	30	262.938	5	320.134	10	370.622	10	454.791
20	142.158	20	177.466	4	221.065	8	263.329	5	321.534	10	371.267	5	457.760
60	142.892	10	177.809	15	222.378	30	263.760	15	322.617	5	375.138*	10	458.709
50	143.033	5	178.286	4	222.718	15	264.029	60	323.816	10	377.355	10	459.511
15	143.634	15	178.489	4	223.368	20	264.414	70	324.485	15	377.756	15	459.881
25	144.728	15	179.223	25	225.497	50	265.641	50	324.607	25	379.326	2	460.653
35	145.651	15	179.630	10	225.991	20	266.061	20	325.038	8	379.573	10	461.319
10	145.671	15	180.384	2	226.785	10	266.584	20	325.687	5	386.943*	10	462.545
100	146.669	20	180.986	10	228.146	10	267.203	20	326.575	8	387.841	20	463.712
20	147.544	30	182.019	6	228.667	25	267.562	15	327.383	3	393.172*	20	464.640
80	148.846	8	182.669	8	230.260	60	268.309	20	327.620	3	394.256*	20	464.824
80	149.703	10	183.396	7	230.451	50	268.773	50	328.412	5	395.202*	15	467.106
26	150.662	7	183.705	2	230.928	40	269.044	25	328.536	30	2–401.346	3	468.505
70	151.429	7	184.938	7	231.833	20	269.653	40	328.737	20	2–401.718	2	468.890
8	152.312	15	186.296	8	232.632	30	270.298	20	328.831	10	2–401.913	20	472.342
8	152.348	5	189.085	4	234.256	20	270.740	100	329.047	8	2–405.921	2	472.775
10	152.383	20	191.719	30	235.299	20	271.443	30	329.805	7	2–406.010	2	474.137
15	152.929	7	192.585	4	235.785	15	272.424	30	329.851	8	2–406.369*	2	474.176
8	152.853	7	193.409	5	236.343	10	272.807	5	330.602*	8	406.439	2	475.500
40	154.785	8	194.050	8	236.714	20	273.417	8	331.573*	5	2–406.860	20	476.201

TABLE III. *Reliability of copper wave-lengths.*

Wave-length region	Comments
109–120A	Poor
120–132A	Fair
132–150A	Consistent (probably fair)
150–240A	Good
240–260A	Consistent (from two plates only)
260–290A	Good
290–302A	From one plate only
302–323A	Good (from two plates only)
323–328A	Good
328–345A	Good (from two plates only)
345–371A	Consistent (probably good)
371–432A	Consistent (two plates only)
432–476A	Poor (two plates only)

length regions followed by characterizing words or phases which indicate the error to be expected in that region. Poor means unreliable data to about ± 0.010A. Fair means that an error of ± 0.005A may be expected and good means that the error is about ± 0.003A. Consistent means that the three sets of data agree well but that the absolute value may be open to question. An asterisk has been placed after lines in Table II which were measured on one plate only.

Unfortunately, the grating used throws very little energy into the second order. Thus only the strongest lines appear in the second order (those preceded by a 2 in Table II at about 400A) and it was impossible to check first and second orders completely. Where a check was possible, first and second order lines agree to about ± 0.003A.

Fig. 1 shows several reproductions of spectrograms with appropriate wave-lengths of Table II designated.

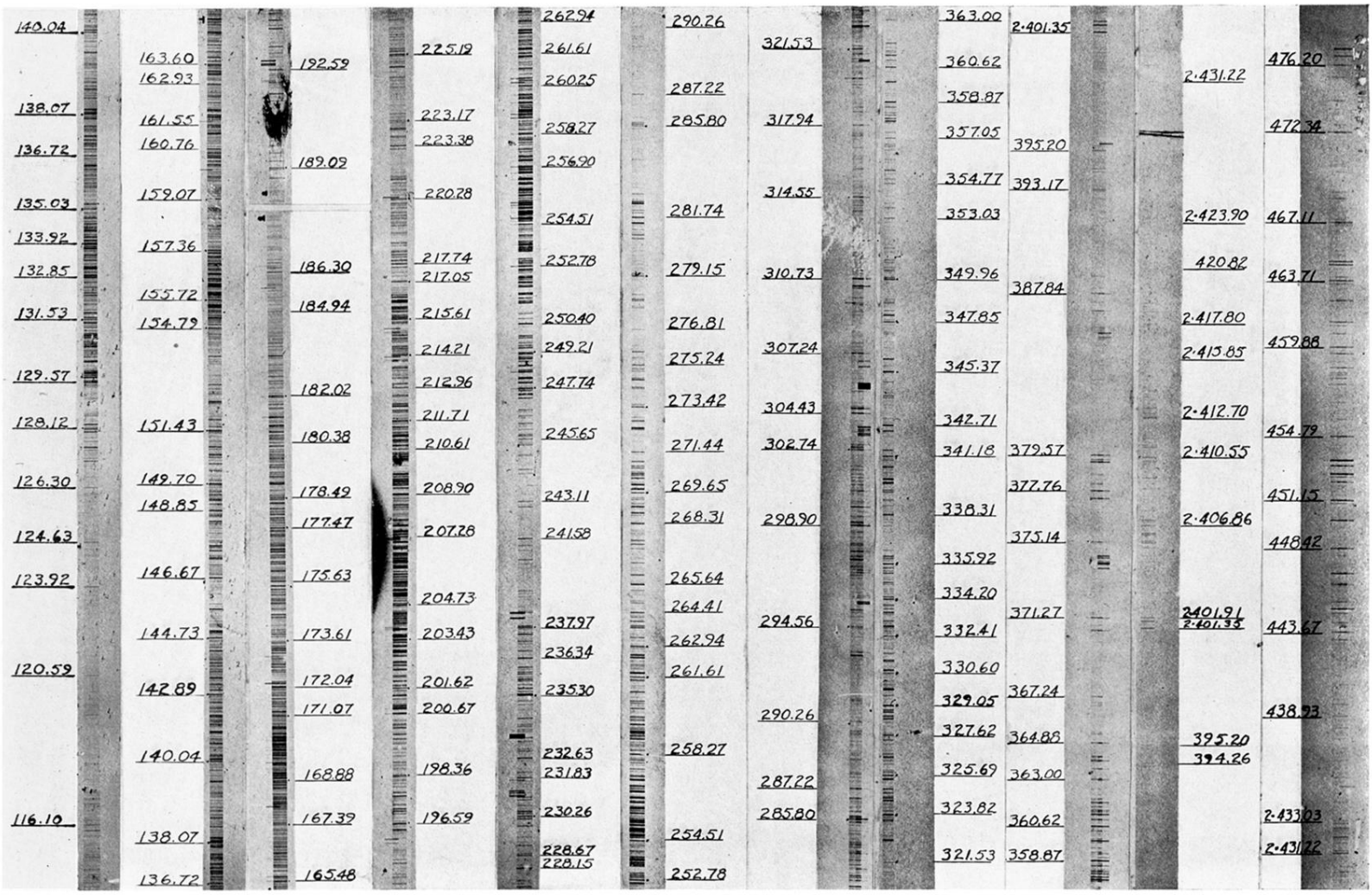

FIG. 1. The copper spectrum with standard lines indicated. Overlapping spectra are due to oxygen, aluminum, and boron.