XIV. *Researches on Spectrum Photography in relation to New Methods of Quantitative Chemical Analysis.*—Part II.

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[Plates 15, 16.]

Introduction.

The first attempt to apply the spectroscope to the quantitative analysis of alloys seems to have been made by the late Dr. W. A. Miller, F.R.S., in the year 1862 (Phil. Trans., Vol. 152, p. 883, 1863, and Jour. Chem. Soc., vol. xvii., p. 82, 1864). By taking photographs of the spectra of alloys of gold and silver of different degrees of fineness he obviously sought to apply this method of working to the assaying of gold. He was at the time an assayer to the Royal Mint. In 1870 M. Janssen proposed two methods of quantitative spectrum analysis. The first was based on measurements of the intensity of the most brilliant rays emitted by incandescent matter, while the second depended upon the time during which a substance emits visible rays during complete volatilisation in a flame (Comptes Rendus, lxxvi., pp. 711–713).

MM. P. Champion and H. Pellet, and also M. Grenier, applied the former spectro-photometrical method with some degree of success to the estimation of alkalies (Comptes Rendus, lxxvi., pp. 707–711). In 1874 Messrs. Lockyer and Roberts attempted and accomplished with a considerable amount of accuracy the determination of the composition of certain tolerably homogeneous alloys of gold and silver, and of lead and cadmium, by means of the spark passed between metallic electrodes, and examined by the spectroscope. The spectrum of the alloy was compared with certain check pieces of known composition. Others who have attempted to make use of emission spectra for the purposes of quantitative analysis are Sir J. G. N. Alleyne, who in 1875 communicated a paper to the Iron and Steel Institute "On the estimation of small quantities of Phosphorus in Iron and Steel by Spectrum Analysis" (Journal of the Iron and Steel Institute, 1875, pp. 62–72), and H. Ballman, who attempted the quantitative estimation of lithium with the spectroscope by observing the degree of dilution of a solution which seemed to cause the extinction of the red line. This is theoretically constant, but practically it varies slightly (Zeitschrift für

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Analytische Chemie, vol. xiv., pp. 297–301; also Journal Chem. Soc., 1876, p. 550, Abstract). Messrs. LIVEING and DEWAR have published notes on quantitative spectroscopic experiments (Proc. Roy. Soc., vol. xxix., pp. 482–489). Observing the emission spectrum of sodium vapour, they sought to estimate the quantity of substance present in a given space by measuring the width of the sodium lines.

It has been already shown that solutions containing the same element in different proportions emit different variations of the same spectrum, the lines differing in number, length, and intensity. I have also proved the converse of this—namely, that, *under the same spark conditions similar solutions of the same strength always emit the same spectrum.* By similar solutions are meant solutions containing salts of the same metal, the non-metallic constituents of which cannot affect the length or strength of the metallic lines. Evidence of a quantitative nature in Part I. has established the fact that chlorides, nitrates, sulphates, and carbonates are salts of a similar character in this respect, and it has also been proved quantitatively in the case of chloride and sulphate of copper. It is, however, doubtful whether solutions of borates and silicates are strictly comparable with the solution of other salts, for the borates and silicates of the alkalies emit strong lines, due to boron and silicon, and it certainly appears, from the observations I have hitherto made, that the metallic spectra are modified by the strong lines of these non-metallic elements.

On the strength and length of lines in the metallic spectra yielded by solutions of various strengths, and on the limit of sensitiveness of the spectrum reaction.

The following investigation was made with the view of placing our knowledge of spectrum analysis on a proper basis, so as to admit of its being applied more systematically than hitherto in the examination of minerals in quantitative analysis, and particularly in the assay of certain metals.

Experiments have been made chiefly on those elements with comparatively simple spectra; those, for instance, which yield a few prominent long lines and many short ones, for since it has been shown that short lines from metallic electrodes become long ones when strong solutions are used, and short again as the solutions are diluted, we may anticipate a greater variety of spectra and a greater range for the exercise of observation, or, in other words, a greater sensitiveness of the spectrum reactions, than with metallic points. As often as possible chlorides have been used in preference to other salts, because hydrochloric acid is the solvent employed most generally in analytical operations, and the chlorides are as a rule the most soluble compounds of the metals, and likely to yield the most highly concentrated solutions. In a few preliminary experiments trial or test-plates were made for use in quantitative analysis, each containing about fifteen photographs of the spectra of solutions of various strengths. It was frequently found desirable to largely increase the number of photographs where gradual alterations in the lines accompanied gradual dilution. Subse-

quently it was deemed necessary to photograph solutions containing 1 per cent., 0·1 per cent., and 0·01 per cent. of the metals, and map the spectra characteristic of each. Other photographs could then be taken as required for comparison with solutions of mineral substances or for estimating the minute constituents of metallurgical products.

To prevent the instrument being splashed with liquid projected outwards by the spark, it is necessary to use a lens in front of the slit, the focal length of which for similar reasons should not be much less than three inches.

In all cases the spark should be regulated in length by passing a piece of plate glass between the electrodes, and adjusting them so that they just touch it. When these conditions are fulfilled and the spark is working properly, a spindle-shaped bundle of rays may be seen when a piece of card is held in the opening of the collimator tube, about two inches behind the slit. The rays which fall upon the centre of the card should not show any wavering motion, for if this be the case the electrodes are not quite in the proper position.

I propose first to describe in detail the changes observable in the spectrum of magnesium when a series of solutions of definite strengths are examined. In the case of other metals detailed descriptions will not be given, but a glance at the maps accompanying this paper which represent both the normal spectra with wave-lengths and the prismatic spectrum with scale numbers for each element, will render the changes in the spectra evident to the eye.

The magnesium spectrum.

The solution examined was prepared by dissolving a weighed quantity of the metal in hydrochloric acid. The changes rendered visible on dilution are the following :—

(1.) *Solution containing* 1 *per cent. Mg., or* 1000 *parts per* 100,000 *of solution.*

The first and third lines of the quadruple group, wave-lengths 2801·6 and 2794·1, are considerably stronger than the second and fourth. Of the quintuple group the lines with wave-lengths 2780·2 and 2776·9 are invisible.

(2.) 0·1 *per cent. Mg., or* 100 *parts per* 100,000 *of solution.*

The least refrangible line, 4480, is shortened by two-thirds. The triplet with wave-lengths 3837·9, 3832·1, and 3829·2 is altered, only one-half of each line is fairly strong, the other half is much weakened.

The triplet with wave-lengths 3096·2, 3091·9, 3089·9 is barely visible, and that through only one-half the length of the lines.

The pair with wave-lengths 2935·9, 2928·2 exhibit a great weakening through two-thirds of their length. The line 2851·3 is fairly strong, one-half being weakened. The second and fourth lines of the quadruple group are much weakened through two-thirds of their length ; wave-lengths of the second 2796·9, of the fourth 2789·6.

Of the quintuple group the first and fifth lines, wave-lengths 2781·8 and 2775·5, are shortened by two-thirds, the third line, wave-length 2778·7, is shortened by one-half. The third is just barely visible as a continuous line when one knows where to look for the weakened portion.

(3.) 0·03 *per cent. Mg., or* 30 *parts per* 100,000 *of solution.*

The least refrangible line, wave-length 4480, has disappeared. The first and third lines of the triplet, wave-lengths 3837·9 and 3831·2, are still visible but very weak.

The second triplet has disappeared.

The doublet, 2935·9–2928·2, is barely a continuous pair of lines, the centres being very much enfeebled. The line 2851·2 is not very much altered, being of equal strength throughout its length instead of having a thickened appearance at one pole.

The quadruple group have not undergone any great change, but the nimbus or halo is extinguished as in the preceding case. Of the quintuple group there is a very faint indication only of the lines with wave-lengths 2781·8 and 2778·7, the others are extinct.

(4.) 0·02 *per cent. Mg., or* 20 *parts per* 100,000 *of solution.*

All the lines are weakened.

The line 2781·8 is extinct.

(5.) 0·01 *per cent. Mg., or* 10 *parts per* 100,000 *of solution.*

The lines are still further weakened, and those with wave-lengths 3837·9 and 3832·1 have become extinct.

The doublet, wave-lengths 2935·9 and 2982·2, is shortened by two-thirds the length of the lines.

The line 2851·2 is attenuated.

Of the quadruple group the second and fourth, wave-lengths 2796·9, 2789·6, are so attenuated as to be barely continuous. Scarcely a trace of the quintuple group is visible.

(6.) 0·001 *per cent. Mg., or* 1 *part per* 100,000 *of solution.*

Of the doublet, the first line is shortened by two-thirds, wave-length 2935·9, the second is weakened and shortened by nearly three-fourths of its length, wave-length 2928·2.

The line 2851·2 is weakened throughout and more especially through one-half its length, it is now barely a continuous line.

Of the quadruple group the first and third lines, wave-lengths 2801·6 and 2794·1, are attenuated through one-half their length to a great degree and are weakened throughout. The second and fourth lines, wave-lengths 2796·9 and 2789·6, are shortened by one-half their length. The difference between this spectrum and that of the solution ten times as strong is shown to be the result of strictly gradationa

changes. Solutions of intermediate strengths yield lines of intermediate length and strength, proportional to the quantity of magnesium present.

(7.) 0·0001 *per cent. Mg., or* 1 *part per* 1,000,000 *of solution.*

The first and third lines of the quadruple group are much attenuated through one-half their length, the other portions being weakened. Copper electrodes were used for this and the following observations on magnesium because the graphite points contained that element in sufficient quantity to give the first and third lines, though not so strongly as this solution.

(8.) 0·00001 *per cent. Mg., or* 1 *part per* 10,000,000 *of solution.*

The same change was noted, the first and third lines being nearly invisible through one-half.

(9.) 0·000001 *per cent. Mg., or* 1 *part in* 100,000,000 *of solution.*

The first and third lines were extinguished as regards one-half their length.

(10.) 0·000,0001 *per cent. Mg., or* 1 *part in* 1,000,000,000 *parts of solution.*

The lines appeared as in the last solution, but they were fainter.

(11.) 0·000,00001 *per cent. Mg., or* 1 *part in* 10,000,000,000 *of solution.*

In this last instance the lines were almost invisible.

This dilution may be regarded as the point of extinction of the most persistent rays of magnesium with the particular spark arrangement I have generally used, or in other words we may easily detect 1 part of magnesium in 10,000,000,000 of liquid. As the quantity of solution utilised by the spark is certainly less than 0·1 cub. centim. we may detect with absolute certainty less than $\frac{1}{100,000,000}$th of a milligram of magnesium.

When the strength of the spark is increased by the use of a much larger coil, and the striking distance between the electrodes is left the same, the strength of the magnesium lines is so altered that with 1 part of the metal in 10,000,000,000 of the solution the two lines with wave-lengths 2801·6 and 2794·1 are rendered as strongly as in the photographs of those obtained with the previous spark arrangement from a solution containing 1 part in 1,000,000 of liquid. The sensitiveness was therefore increased ten thousandfold. We have thus sufficient evidence to show that the sensitiveness of the spectrum reaction in this case is practically without limit. It varies however with different metals.

TABULAR Description of the Spectra characteristic of Solutions containing Magnesium.

Scale numbers.	Wave-lengths of the principal lines visible.	Parts of magnesium per 100,000 of solution.							
		1,000	100	30	20	10	3	2	1
Hundredths of an inch.									
17·46	4480	*	*						
59·30	3837·9	*	*	*	*				
59·83	3832·1	*	*	*	*				
60·07	3829·2	*	*						
142·3	3096·2	*	*						
142·85	3091·9	*	*						
143·18	3089·9	*	*						
168·7	2935·9	*	*	*	*	*	*	*	*
170·18	2928·2	*	*	*	*	*	*	*	*
184·63	2851·2	*	*	*	*	*	*	*	*
194·55	2801·6	*	*	*	*	*	*	*	*
195·39	2796·9	*	*	*	*	*	*	*	*
195·95	2794·1	*	*	*	*	*	*	*	*
196·92	2789·6	*	*	*	*	*	*	*	*
198·64	2781·8	*	*	*					
198·96	2780·2								
199·3	2778·7	*	*	*	*	*			
199·61	2776·9								
199·97	2775·5	*	*						

The following tables, together with the maps of the lines, are considered to be sufficiently descriptive of the different spectra. The wave-lengths of the lines characteristic of each solution are given in separate columns.

THE Zinc Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
108·49	3344·4	3344·4	3344·4
113·75	3301·7	3301·7	3301·7
116·30	3281·7	3281·7	3281·7
145·69	3075·6	3075·6	
194·98	2800·1	2800·1 ?	
252·31	2557·3	2557·3	
267·95	2501·5	2501·5	

The most persistent lines of zinc are probably those of high refrangibility which do not ordinarily appear when gelatine emulsion plates of the kind most generally used are employed.

* Lines which are visible. A line may be shortened or weakened, but an asterisk opposite to its wave-length in this table denotes that although it may be changed it is still visible. Only the first, third, and fifth lines of the quintuple group have been mapped.

The Cadmium Spectrum.

Scale numbers.	Wave-lengths.			
	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
Hundredths of an inch.				
79·37	3612·0	3612·0	3612·0	
79·68	3609·6	3609·6	3609·6	
94·30	3466·7	3466·7	3466·7	
94·50	3465·2	3465·2	3465·2	
101·45	3402·8	3402·8		
119·0	3260·2			
205·87	2747·7	2747·7		
248·24	2572·3	2572·3		
326·8	2321·6			
329·85	2313·5	2313·5	2313·5	
339·25	2288·8	2288·8	2288·8	
348·15	2265·8	2265·8	2265·8	2265·8
377·48	2196·4			
400·2	2146·8			

The Aluminium Spectrum.

Scale numbers.	Wave-lengths.			
	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
Hundredths of an inch.				
49·85	3960·9	3960·9	3960·9	3960·9 ?
51·16	3943·4	3943·4	3943·4	3943·4 ?
The air lines contiguous to the above are very strong, hence it is a little doubtful whether they are present in the spectrum of a solution so dilute as 0·001 per cent.				
70·02	3713·4			
71·05	3701·5			
79·17	3612·4	3612·4	3612·4	
80·5	3601·1	3601·1	3601·1	
82·07	3584·4			
142·86	3091·8	3091·8	3091·8	3091·8
144·5	3081·2	3081·2	3081·2	3081·2
148·5	3056·6			
191·76	2815·3	2815·3	2815·3	2815·3
226·3	2659·3	2659·3		
228·26	2651·2	2651·2		
249·66	2566·9	2566·9		
308·55	2373·3			
309·0	2372·0			
309·6	2370·2			
309·94	2367·2			
310·62	2364·5			

The line with wave-length 3584·4 is both *much longer* and *stronger* than either

3612·6 or 3601·2, yet it is not so persistent. From appearing as a strong line it disappears rather suddenly.

The line with wave-length 2815·3 is the strongest in this spectrum.

The Indium Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
15·88	4510·2	4510·2	
39·91	4101·3	4101·3	
119·31	3257·8		
119·68	3255·5	3255·5	3255·5
151·35	3038·7	3038·7	3038·7
168·00	2940·8	2940·8	
177·34	2889·7	2889·7*	
214·56	2709·3	2709·3	
251·76	2559·5		
332·2	2307	2307	

The Thallium Spectrum.

Scale numbers.	Wave-lengths.		
	1·0 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
64·55	3775·6	3775·6	3775·6
88·7	3518·6	3518·6	
143·0	3091·0	3091·0	
172·21	2917·7		
201·87	2767·1	2767·1	2767·1
259·86	2530·0	2530·0	
335·27	2299·3	2299·3	

* This is barely visible.

The Copper Spectrum.

Scale numbers.	Wave-lengths.			
	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
Hundredths of an inch.				
113·10	3306·8	3306·8		
115·10	3289·9			
117·25*	3273·2	3273·2	3273·2	
120·7	3246·9	3246·9	3246·9	3246·9
164·53	2959·5			
190·13	2823·2			
201·36	2769·1	2769·1		
211·8	2721·2			
212·55	2718·4	2718·4		
213·7	2713·0	2713·0		
216·1	2702·7			
216·58	2700·5			
219·37	2688·8	2688·8		
224·7	2666·7			
236·45†	2617·8			
241·1	2599·7			
241·58	2598·3			
255·94	2544·6	2544·6		
260·25	2528·8	2528·8		
261·00	2526·2			
266·77	2506·2	2506·2		
270·91	2491·4			
271·65	2489·1			
272·72	2485·6			
276·45	2473·2			
298·31	2403·3			
299·4	2400·1			
309·17	2371·6	2371·6		
309·57	2370·1	2370·1		
336·8	2295·0			
343·67	2277·0			
355·27‡	2248·2	2248·2		
355·5	2247·7	2247·7		
357·1	2244·0	2244·0		
357·32	2243·5	2243·5		

* This pair of lines differs from all others in the spectrum by not being shortened on dilution, but becoming attenuated till at last they disappear. They remain long lines till the last.

† This is a very fine and very long line.

‡ This group is distinctly seen to be composed of four lines in the photographs of the 1 per cent. solution, and some lines, to the number of four or five, more refrangible than these are visible

The Silver Spectrum.

Scale numbers.	Wave-lengths.			
	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
Hundredths of an inch.				
103·94	3382·3	3382·3	3382·3	
116·45	3280·1	3280·1	3280·1	
168·5	2937·5			
169·3	2933·5	2933·5		
170·17	2928·2	2928·2		
175·02	2901·6			
176·07	2895·6			
180·44	2872·7	2872·7		
191·82	2814·5			
195·03	2798·8			
201·81	2766·4	2766·4		
204·2	2755·5			
214·22	2711·3	2711·3		
226·27	2659·6	2659·6		
227·08	2656·2			
246·3	2579·9			
268·81	2506·0	2506·0		
274·52	2479·9			
275·41	2476·8			
276·41	2473·3	2473·3		
279·92	2462·2			
280·52	2459·8			
282·6	2453·0			
284·38	2447·4	2447·4		
287·46	2437·3	2437·3	2437·3	
290·0	2429·8	2429·8		
293·08	2419·9	2419·9		
295·35	2413·3	2413·3	2413·3	2413·3
295·94	2411·3	2411·3		
297·94	2406·4			
298·85	2404·5			
301·10	2395·7			
302·74	2390·8			
304·07	2386·7			
305·25	2383·6			
307·94	2375·5			
311·70	2364·3			
312·34	2362·3			
313·47	2359·2	2359·2		
313·88	2358·0	2358·0		
323·35	2331·7	2331·7	2331·7	
325·73	2325·3	2325·3	2325·3	
327·37	2320·5	2320·5	2320·5	
328·59	2317·4	2317·4	2317·4	
342·55	2280·7	2280·7		
354·95	2249·9	2249·9		
354·90	2247·6	2247·6	2247·6	
362·86	2230·6			

The Mercury Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
74·6	3662·9		
75·37	3654·4		
77·37	3632·9	3632·9	
137·95	3124·5		
137·08	3130·4	3130·4	
163·37	2966·4	2966·4	
185·45	2846·8		
258·75	2533·8	2533·8	2533·8
364·51	2225·7		

The Tin Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
62·40	3800·3	3800·3	
107·51	3351·8	3351·8	
110·25	3329·9	3329·9	
116·03	3282·9	3282·9	
118·83	3261·6	3261·6	
130·7	3174·3	3174·3	
152·18	3033·0	3033·0	
156·29	3007·9	3007·9	
173·05	2912·0		
176·18	2895·0		
177·8	2886·9		
182·47	2862·0	2862·0	2862·0
184·99	2849·2		
187·01	2833·9	2833·9	
192·3	2812·5	2812·5	
198·28	2784·0		
199·34	2778·8	2778·8	
215·35	2705·8	2705·8	2705·8
224·95	2664·2		
225·98	2660·6		
226·56	2657·9	2657·9	
229·67	2645·4		
230·23	2643·2	2643·2	
233·17	2631·4	2631·4	
242·65	2593·6		
243·10	2591·7		
248·70	2570·5	2570·5	
255·45	2545·6	2545·6	
269·8	2495·0		
273·4	2482·9	2482·9	
289·95	2429·3	2429·3	2429·3
292·37	2421·8	2421·8	
310·11	2368·3		
314·85	2355·0	2355·0	
321·94	2335·3		
328·34	2317·9		
355·83	2247·0		

The Lead Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
42·93	4057·5	4057·5	
67·61	3738·9	3738·9	
72·69	3682·9	3682·9*	
76·8	3639·2	3639·2	
83·31	3572·6	3572·6	3572·6
170·45	2872·2	2872·2†	
188·37	2832·2	2832·2	
190·30	2822·1		
225·41	2662·5	2662·5	
237·48	2613·4	2613·4	
247·08	2576·4		
373·43	2204·3		

The Tellurium Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
103·9	3382·4	3382·4	
116·43	3280·0	3280·0	
117·35	3273·4	3273·4	
120·77	3246·8	3246·8	3246·8
176·24	2894·3		
181·25	2867·7		
183·4	2857·0		
344·1	2386·3	2386·3‡	
304·92	2383·8	2383·8‡	
355·18	2248·0		
355·36	2247·3§		
357·18	2243·3		

The Arsenic Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
183·04	2859·7		
199·22	2779·5	2779·5	
316·6	2350·1		
339·14	2288·9		

This is an exceedingly poor spectrum.

* Barely visible. † Very faint.
‡ These lines appear very distinctly and are continuous in a 1 per cent. solution.
§ The two last lines are faint, 2243·3 exceedingly so.

The Antimony Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
Hundredths of an inch.			
67·63	3739·0		
80·74	3597·8		
90·21	3504·6		
109·36	3336·4		
118·21	3266·6		
120·8	3246·6		
122·87	3231·6		
152·91	3029·0		
179·29	2877·1	2877·1	2877·1
197·05	2789·6	2789·6	
241·65	2597·2	2597·2	2597·2*
260·33	2527·6	2527·6	
330·37	2311·8		

The Bismuth Spectrum.

Scale numbers.	Wave-lengths.		
	1 per cent.	0·1 per cent.	0·01 per cent.
undredths of an inch.			
63·1	3792·7		
71·63	3695·3		
80·99	3595·7		
89·69	3510·5		
98·4	3430·9		
102·25	3396·7		
146·85	3067·1	3067·1	3067·1
153·75	3023·8	3023·8	
158·98	2992·2	2992·1	
159·67	2988·1		
168·52	2937·5		
175·85	2897·2	2897·2	
183·91	2854·8	2854·8	
185·49	2846·1	2846·1	
294·66	2414·8		

* There is a little doubt whether this is actually the line observed, as the scale number was omitted at the time the notes were written, and the line had the wave-length 2579·1 assigned to it, which is obviously incorrect, as no line with such a wave-length appears on my maps.

It has been shown by M. LECOCQ DE BOISBAUDRAN that when the temperature of a source of light (flame or spark) is increased, the *relative* intensity of the more refrangible rays is much increased; the *absolute* brilliancy of the less refrangible rays sometimes undergoes a diminution which may even amount to extinction (Comptes Rendus, vol. lvxxiii., p. 943). It must not be inferred that photographs of spark spectra produced precisely in the manner here described are liable to variations in the relative intensities of their lines or the order in which they disappear as the quantity of substance in the spark decreases. I have observed the invariable character of the cadmium, tin, lead, and magnesium lines in about five thousand photographs, including not fewer than two hundred examples of other metals, all being obtained for various purposes in the course of seven years' work under such variable conditions as may be introduced by the electrodes being near together or far apart, or by the use of a large or small coil, but with a condenser of the same size always in circuit. The reason of this constancy is sufficiently obvious when we consider that unless the spark be almost at the highest temperature attainable the emissive power is insufficient to affect the sensitive plate in the usual period of time; when there is a slight fall in temperature there is a shortening of all lines such as is caused by a diminished period of exposure.

The method of using these tables.

The scale numbers given in the first column of the tables are linear measurements of the positions of the lines in the different prismatic spectra, photographed copies of which have been published in the Journal of the Chemical Society, vol. xli., p. 84. They serve two purposes, first as a check upon the wave-lengths quoted, and secondly as a means of identifying the lines. Suppose, for instance, I wish to identify the line in the indium spectrum which is mapped as double, it will be seen that the least refrangible line stands at nearly 16, and the next at as nearly as possible 40 on the scale. Applying an ivory rule to the photograph (*loc. cit.*), the rule being divided into hundredths of an inch, so that the numbers 16 and 40 correspond with the two least refrangible lines, it will be found that a very strong line stands at 120, and it is this which appears as double on the map, though the fact cannot be seen by examination of the printed photographs. A reference to the table will show that at 119·31 and 119·68 on the scale there are two lines with wave-lengths 3257·8 and 3255·5, the former of which does not appear in solutions containing $\frac{1}{10}$th per cent. of the metal, while the latter continues visible even when only $\frac{1}{100}$th per cent. is present. The tables of scale numbers and wave-lengths are of little value, however, without the maps. As an illustration of the way in which the maps may be used, let us suppose that a sample of pyrites cinder is being examined for copper and silver. It will be seen at a glance that the most persistent group of characteristic lines in the spectrum of silver lies between wave-lengths 2300 and 2500, those lines situated in a position

corresponding to wave-length 2250 being liable to be confounded with the copper lines at the same point, and one of the less refrangible lines of silver being also liable to confusion with a group of copper lines with wave-lengths lying between 3245 and 3310. Referring to the table we get the exact wave-lengths of the lines and their position on the scale, so that they may be identified at once on a photographed prismatic spectrum. A similar reference to the silver and lead maps and tables will at once tell us the exact position of those lines which are to be sought for in a specimen of argentiferous lead. In very many cases the character of the lines is sufficient to identify them, provided we know something of their position. It may not be without interest if a description of the method of working which I have adopted be made to serve as the conclusion of this portion of the paper.

An estimation of beryllium.—A preparation of ceric phosphate was examined in order to establish beyond all doubt that it was of great purity. A 10 per cent. solution of the substance in hydrochloric acid yielded photographs in which none but cerium lines were visible, with the exception of one single line with a wave-length 3130·2 belonging to beryllium. A solution of beryllium oxide containing $\frac{1}{1000}$th of the metal was diluted to 100 times its original volume before its spectrum was comparable with that of the ceric phosphate. It was then seen that the line with the wave-length 3130·2 was much stronger than in the photograph of the ceric phosphate. It was therefore considered proved that the preparation contained less than 0·01 per cent. of beryllium.

The analysis of an amygdaloid limestone.—The complete qualitative and quantitative analysis of a mineral as far as regards the bases present was carried out in the following manner. The substance, which we will call mineral (*a*), consisted of small almond-shaped masses apparently of the nature of zeolites interspersed with a highly crystalline and almost transparent material considered to be the matrix. It effervesced with acids, dissolving completely and yielding no residue of silica, a result which was quite unexpected. After evaporation to dryness, twice repeated, there was even then no appreciable quantity of silica. A strong solution containing 20 per cent. of the solid was submitted to the spectroscope; the calcium lines came out prominently in the photograph, and in addition the quadruple and the quintuple groups of magnesium were noticeable, but no other metallic lines. Magnesium being in much the smaller proportion was estimated first.

The estimation of magnesium.—One gram of the mineral was dissolved in hydrochloric acid and made up to 100 centims. by volume. The solution yielded a spectrum with closest possible resemblance to that on the test-plate rendered by a solution containing $\frac{1}{10,000}$th of the metal. Three separate solutions were made containing 1, 2, and 3 parts of the mineral in 1000 volumes of the solution. These were photographed on one plate. On comparison with the standard photographs it was found that they exactly corresponded to those obtained from solutions containing 1, 2, and 3

parts of magnesium in 100,000 volumes of solution. The mineral, therefore, was considered to contain 1 per cent. of magnesium. The comparison of the photographs was made by three independent observers who each gave the same figures* from two different series of photographs. By simple inspection of the first photograph the calcium was seen to be present to the extent of something between 30 and 40 per cent. of the mineral. The more precise estimation of this mineral presented some difficulties, both on account of the mineral containing this element as its chief constituent, and by reason of the fact that dust floating in the air is apt to contaminate the electrodes with calcium, but not with magnesium. The hydrochloric acid used likewise always shows this substance to be present.

The estimation of calcium.—A series of solutions of calcium chloride were made containing the following proportions of calcium: $\frac{1}{1000}$th, $\frac{1}{2000}$th, $\frac{1}{3000}$th, $\frac{1}{4000}$th, $\frac{1}{5000}$th, $\frac{1}{10,000}$th, $\frac{2}{10,000}$th, $\frac{3}{10,000}$th, $\frac{4}{10,000}$th, $\frac{5}{10,000}$th, $\frac{3}{100,000}$th, $\frac{4}{100,000}$th, and $\frac{5}{100,000}$th.

The first photograph of the mineral, which was taken from a solution containing 1 gram dissolved in hydrochloric acid and made up to 1 litre, exhibited a spectrum, the length and strength of the lines in which indicated between 1 and 2 parts of calcium in 4000 of liquid. The solution of the mineral containing 1 in 10,000 corresponded very closely with 3 in 100,000 of the calcium solution, or about 30 per cent.

On account of the strength of the calcium lines and the occasional vitiation of the results by calcium in floating dust, it was deemed advisable to shorten the period of exposure from two minutes to half a minute.

The next photograph showed that 4 in 100,000 of calcium solution was stronger than 1 in 10,000 of the mineral. There is therefore less than 40 and more than 30 per cent. calcium in the mineral.

Photographs of the calcium solution were then taken containing 3·5 centims., 3·6 centims., 3·7 centims., 3·8 centims., and 3·9 centims. of the standard solution in 100 centims., or 3·5 parts per 100,000 and so on.

Photographs were then taken with a quarter and with half a minute's exposure, which was found sufficient; even five seconds gave very fair indications of the calcium lines.

The solution of the mineral containing $\frac{1}{10,000}$th was then treated in the same way; the results are as follows:—

* To speak more particularly, the photographs were taken by Mr. Templeton, a student in the Royal College of Science, and his results were checked by Mr. W. E. Adeney, the Assistant Chemist, and by myself. A second series of photographs was also taken by myself.

The mineral. $\frac{1}{10,000}$	The standard solution. $\frac{3{\cdot}7}{100,000}$
(1) Five seconds' exposure.	(1) Five seconds' exposure.

The stronger.

(2) Fifteen seconds' exposure.	(2) Fifteen seconds' exposure.

The least refrangible pair of lines H and K in the one photograph are of equal strength to those in the other. The most refrangible pair of lines are a little stronger in the standard solution than in the mineral.

(3) Thirty seconds' exposure.	(3) Thirty seconds' exposure.

The least refrangible pair of lines in the mineral solution appear not quite so strong as those of the standard solution.

(4) Five seconds' exposure.	(4) Five seconds' exposure.
(5) Fifteen seconds' exposure.	(5) Fifteen seconds' exposure.

These two series of photographs were compared, but no difference could be observed between them, hence it was concluded that 37 per cent. of calcium was contained in the mineral.

This was not considered to be the *exact* proportion, because the lines had not been reduced sufficiently by dilution to give a good indication of the differences between solutions of approximately the same composition. It would not have been possible to carry further dilution into practice because of the complications introduced by the dust in the air. It is needless to say that carbon electrodes were not employed for the later experiment but points of gold. If we calculate the composition of the mineral as thus ascertained we arrive at the following numbers :—

	Per cent.			Per cent.
Mg. . .	1	=	$MgCO_3$. . .	3·5
Ca. . .	37	=	$CaCO_3$. . .	92·5
			Total soluble carbonates	96·0

Two analyses made in the ordinary manner by an independent analyst gave the figures which here follow. The separation of the magnesia was made with all possible care according to the directions of FRESENIUS,* a correction being introduced for the solubility of the ammonia-magnesian phosphate in the filtrate and wash-water.

	Per cent.			Per cent.
(1) Magnesium .	1·17	=	$MgCO_3$.	4·08
Calcium . .	36·45	=	$CaCO_3$. .	91·11
			Total carbonates .	95·19

* English Edition, by J. LLOYD BULLOCK and ARTHUR VACHER, 1865, pp. 632, 273, and 167.

The portion examined as stated above contained no iron or alumina, only an insoluble residue in addition to the carbonates. The following analysis shows a slightly different composition :—

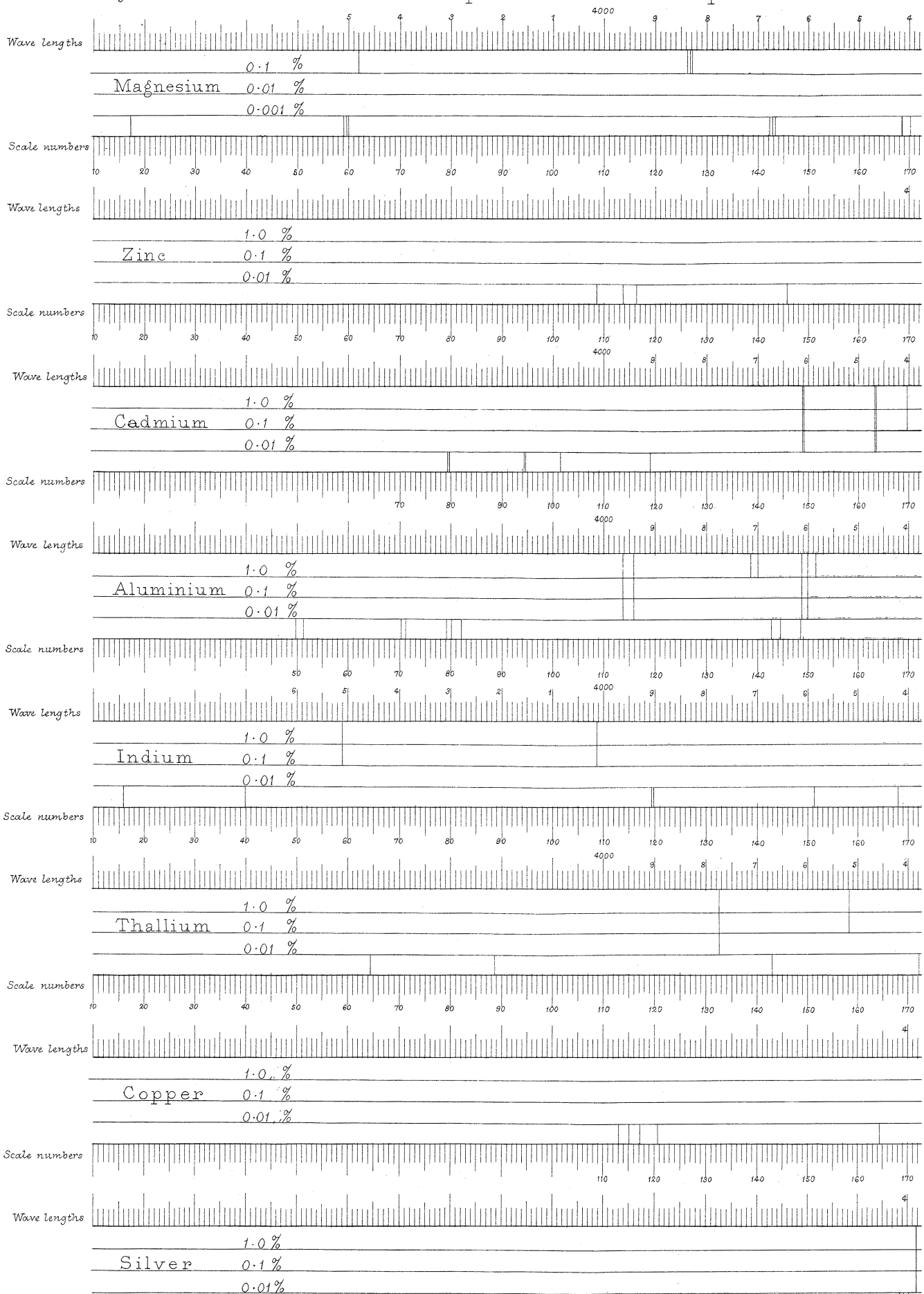
	Per cent.			Per cent.	Total carbonates.
(2) Magnesium . .	1·38	=	$MgCO_3$. .	4·83	97·28
Calcium . .	36·98	=	$CaCO_3$. .	92·45	
Fe_2O_3 and Al_2O_3		=		2·24	
Insoluble residue		=		0·82	
			Total	100·34	

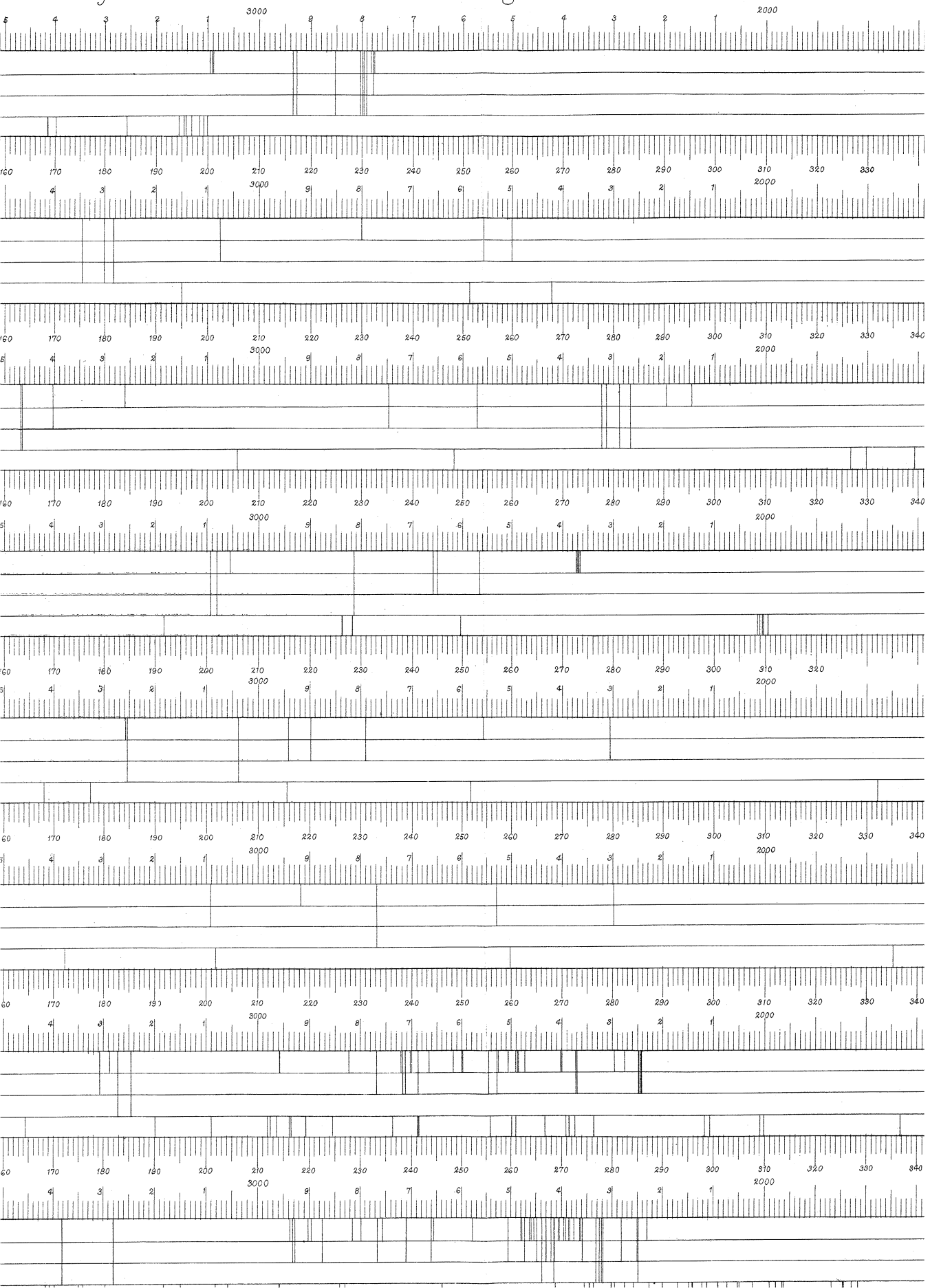
Estimations of copper.—Several estimations of copper were made with great success when the metal was present in not greater proportion than 5 or 6 per cent. Thus 3·8 per cent. and 4·2 per cent. were numbers identical with those obtained by the ordinary process of analysis of two specimens of pyrites. It is not, however, apparent that there is any advantage in estimating copper in this way, since although it may be sufficiently accurate and speedy, there are volumetric processes which are quite as satisfactory in this respect, and capable of execution with simpler apparatus.

The spectroscope is only applicable in certain cases with advantage; when, for instance, it enables one to dispense with elaborate processes of separations and repeated weighings. I hope in a future communication to place on record the method of executing special assays in a perfectly satisfactory manner.

Hartley.

Maps of Metallic Spectra Emitted

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2000
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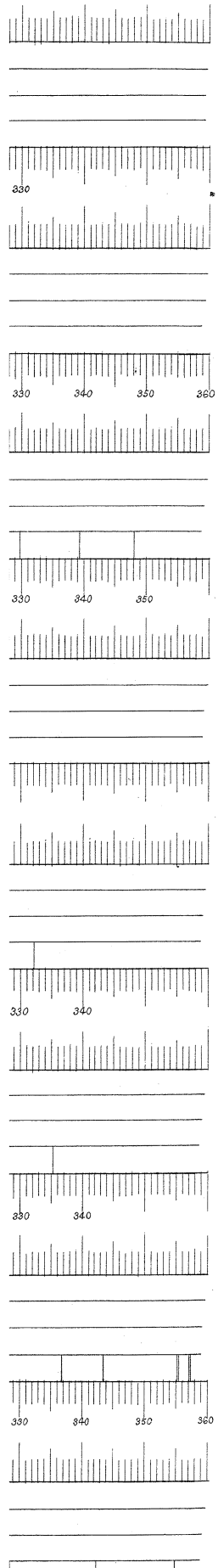
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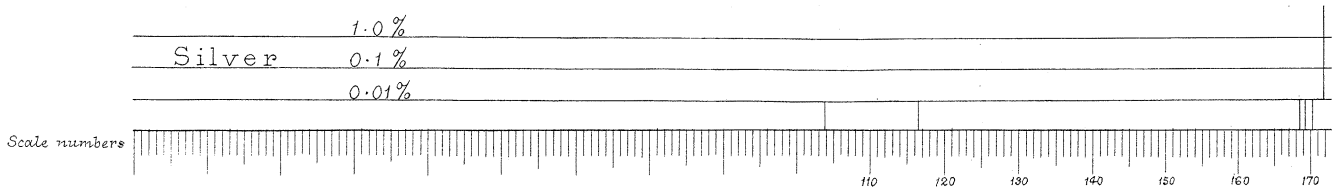
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0·1 %
0·01 %
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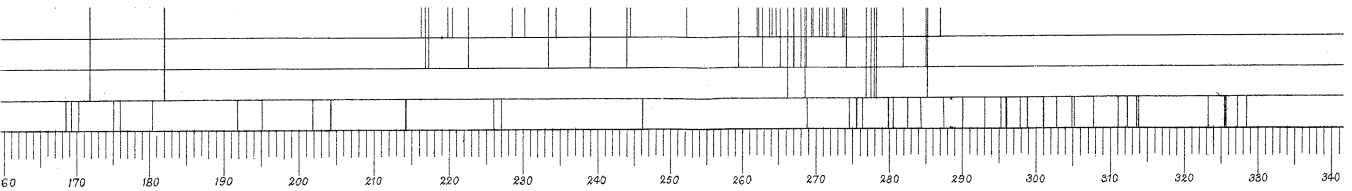
130
140
150
160
170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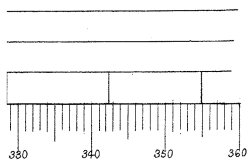
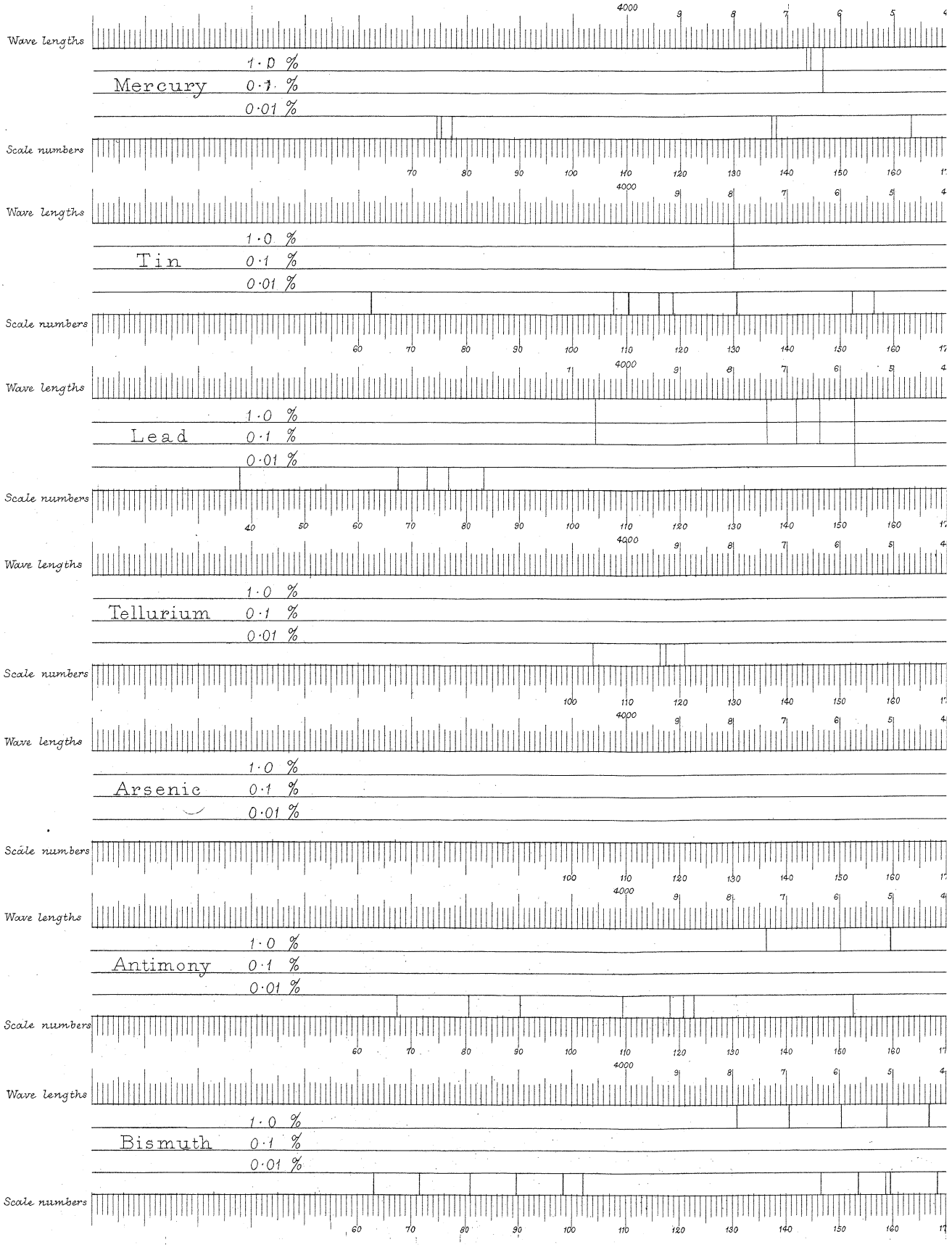
340

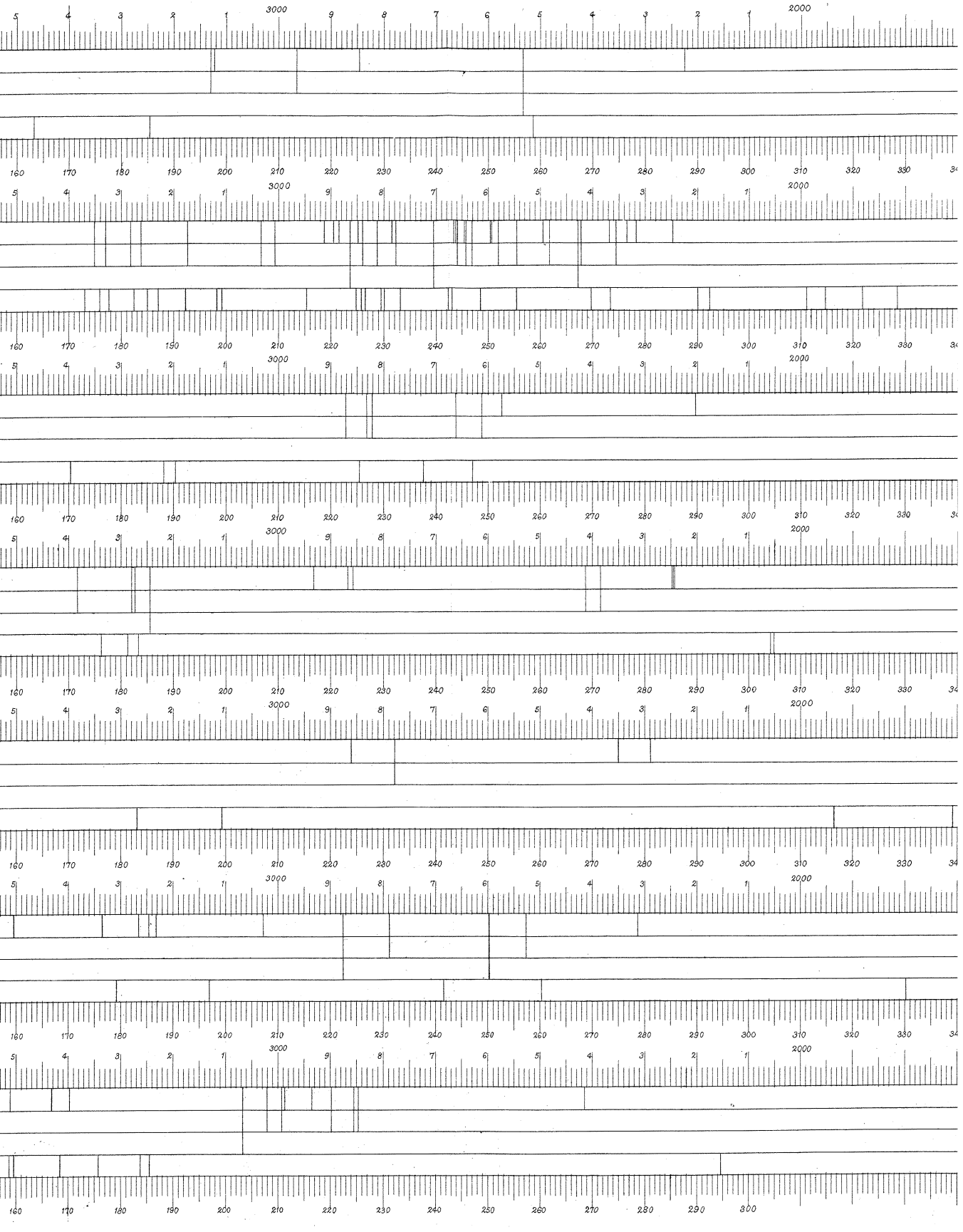
West N



West Newman & Co sc.

Maps of Metallic Spectra Emit

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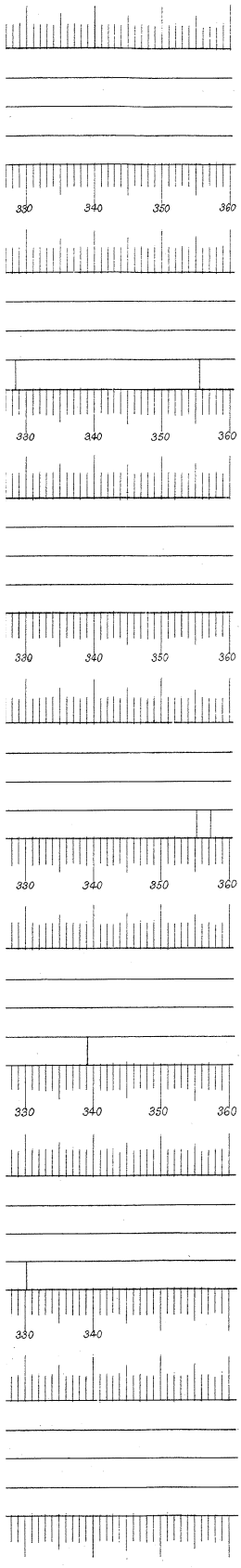
1884. *Plate* **16.**



West Newman & Cº sc.

Maps of Metallic Spectra Emitted by Solutions of Definite Strengths.

West, Newman & Co. imp.

Maps of Metallic Spectra Emitted by Solutions of Definite Strengths.

Phil. Trans. 1884. *Plate* 16.

West, Newman & Co. imp.