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On Scandium

William Crookes

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II. *On Scandium.*

By Sir WILLIAM CROOKES, *D.Sc.*, *F.R.S.*

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[PLATE 1.]

SCANDIA is one of the rarest and least known of the recognised rare earths. It was discovered in 1879 by NILSON, who separated it, with ytterbia, from erbia extracted from euxenite and gadolinite. NILSON made an incomplete chemical examination of some of its compounds, but owing to the inadequate amount of material at his disposal he did not at first entirely separate it from ytterbia. Later in the same year CLEVE extracted scandia from gadolinite, yttrotitanite, and keilhauite, and described the scandium sulphate, double sulphates, nitrate, oxalate, double oxalates, selenate, acetate, formate, oxide, and hydrate, and gave some of the chief reactions of the new body.

CLEVE, working on gadolinite, found that it contained only from 0·002 to 0·003 per cent. of scandium, while keilhauite yielded only about 0·005 per cent. He gave results from which he deduced an atomic weight of about 45. CLEVE noticed that scandium almost exactly corresponded to the description given by MENDELEEFF of his hypothetical element "ekaboron," of atomic weight 44. More recently, in 1880, NILSON, working on somewhat larger quantities of scandia, described and analysed the nitrate, sulphate, selenate, oxalate, and the potassium double sulphate. He found the atomic weight to be 44·03, the mean of four separate and closely concordant determinations. Taking NILSON'S data, and re-calculating from them the atomic weight of scandium, using the most recent figures for oxygen and sulphur, I find his atomic weight to be almost exactly 44·1—a figure I have used in the following paper.

In the course of my 20 years' work on the fractionation of the rare earths I have repeatedly tested my products by examining their photographed spectra, using the dominant lines of the various elements as tests for their presence. Scandium has an extremely characteristic group of lines in its spectrum, situated between wave-length 3535·864 and wave-length 3651·983, the strongest being at 3613·984, midway between two strong iron lines. By using a part of the spectrum in which this line occupies the centre of the photograph, it is easy to recognise scandium. Detecting the dominant line, the presence of scandium can be verified by reference to the other lines of the group. (See the plate at the end of this paper.)

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* The descriptions and analyses of the Fluoride, Succinate, Benzoate, the Toluates, Phenyl-acetate, Pyromellitate, and Camphorate were received June 25, 1908.

Scandium I found in some of my fractions, but only in small quantities. A few years ago I commenced an examination of all the obtainable rare-earth minerals, in order to see if any of them showed more than a trace of scandium. The minerals examined were:—

Æschynite
Allanite
Alvite
Auerlite
Baddeleite (Ceylon)
Bastnasite
Bröggerite
Cerite
Cleveite
Columbite
Cryptolite
Eudialite
Euxenite
Fergusonite (Ceylon)
Fergusonite (Ytterby)
Fluocerite
Gadolinite
Hielmite
Homolite
Keilhauite
Knopite
Koppite
Lanthanite
Monazite
Mosandrite
Orangite
Orthite
Polycrase
Pyrochlore
Rhabdophane
Samarskite
Scheelite (Bohemia)
Scheelite (New Zealand)
Schorlomite
Sipylite
Tantalite
Thalenite
Thorianite
Thorite
Thorogummite
Tscheffkinite
Tysonite
Urdite
Wiikite
Xenotime
Yttergarnet
Yttrialite
Yttrocerite
Yttrogummite
Yttrotantalite
Yttrotitanite
Zirkelite (Ceylon, sp. gr. 5·0)
Zirkelite (Ceylon, sp. gr. 4·42)

Of these minerals scandium was detected in auerlite, cerite, cryptolite, keilhauite, koppite, mosandrite, orangite, orthite, pyrochlore, thorianite, thorite, urdite, and wiikite. But while the other minerals contained less than 0·01 per cent. of scandium, wiikite was found to contain more than one hundred times that amount.

Wiikite is a black amorphous mineral found with monazite in a felspar quarry at Impilaks, Lake Ladoga, Finland. It is named after Professor Wiik, of Helsingfors (‘Min. Mag.,’ vol. xiii., p. 379).

I have compared wiikite with a large number of typical rare-earth minerals, and in appearance I find it most resembles yttrotantalite. A thin section under the microscope looks like solidified mud. It is quite amorphous, breaks with a conchoidal fracture, shows no crystalline structure, and has no action on polarised light.

Wiikite is somewhat radio-active. A fragment was laid on a sheet of sensitive film—opaque black paper intervening—for ninety-five hours. Subsequent development revealed a good impression, about equal in strength to what would be given by pitchblende in twenty-four hours. The image was not uniform, and at one point radiation had spread from the mineral over the adjacent part of the sensitive film.

The specific gravity of wiikite is 4·85. Its hardness is 6. It is infusible before the blowpipe. It is imperfectly attacked by strong mineral acids and breaks up easily when fused with potassium bisulphate. Heated to full redness in a silica tube it gives off helium, water, and a distinct amount of sulphuretted hydrogen, followed by a white sublimate. The mineral begins to crack at a temperature a little below redness, and, at the approach of redness, gas is evolved with almost explosive violence, the mineral breaking and flying about the tube. A fragment so treated examined under the microscope shows a surface covered with glistening points. With a high power these points are resolved into a mass of minute cubes, curiously regular in form and appearance. Heating drives off 5·83 per cent. of its weight; 5·82 of the loss is water and acid vapour, the difference, 0·01 per cent., consists chiefly of helium, with a little hydrogen, carbon dioxide, and a mere trace of neon. The average amount of gas collected from 100 grs. of the mineral was 15·6 cc. Sir JAMES DEWAR kindly passed the gases for me over hot oxide of copper and then through charcoal immersed in liquid air. This should absorb and retain everything but helium and the trace of neon. The gas thus purified, after exhaustion to the most luminous point, was sealed in a double-bulb silica tube. The spectrum, visual and photographed, was that of pure helium with a scarcely perceptible trace of neon.

Containing so many bodies, the exact separation of which one from the other is not known, it is at present impossible to give an accurate and complete analysis of wiikite. Moreover, I find the composition varies somewhat in different samples of the mineral. The following is considered a fair approximation of the composition of a typical specimen :—

Tantalic acid with some niobic acid	15·91
Titanic acid and zirconia	23·36
Earths of the cerium group	2·55
Earths of the yttrium group	7·64
Scandia	1·17
Thoria	5·51
Ferrous oxide	15·52
Uranic oxide	3·56
Silica	16·98
Water and gases	5·83
Calcium, manganese, tin, sulphur, &c., unestimated	1·97
	100·00

The percentage of scandia is too low. Owing to the difficulty of separating it completely from the accompanying earths and metallic acids, the amount given is only that which has been obtained in an approximately pure state.

I find the following the best process to extract scandia from wiikite :—The ground mineral is passed through an 80-mesh sieve, then mixed with five times its weight of powdered potassium bisulphate and fused in a clay crucible. At first much frothing occurs, due to the escape of permanent gases and aqueous vapour; this ebullition can be abated by stirring with an iron rod. When in quiet fusion, the heat is raised to full redness for ten minutes and the liquid mass poured on an iron plate.

When cold, the melt is finely ground, mixed with water in the proportion of 1 kilo. to 5 litres, and mechanically agitated for about twelve hours. It is then thrown on a linen filter and well washed. This treatment extracts most of the rare earths, together with a little titanic, niobic, and tantalic acids and zirconia, but the bulk of these bodies is left behind.

The solution is supersaturated with ammonia and well boiled; this treatment precipitates all the earths, together with iron, titanic acid, zirconia, &c. The precipitate of crude earths is filtered and well washed.

The precipitated crude earths are converted into oxalates by heating the pasty precipitate in a dish with crystals of oxalic acid added gradually, excess being avoided as much as possible. When cold, the oxalates are filtered off, and the iron, &c., in the filtrate is precipitated with ammonia. As scandium oxalate is slightly soluble in water, the iron precipitate will contain a certain proportion, which must be kept for subsequent working up.

The washed oxalates are dried and ignited; the resulting earths form about 17 per cent. of the mineral and contain about 7 per cent. of scandia.

The crude oxides are converted into sulphates by heating with sulphuric acid, the excess of acid being driven off by heat—not using too high a temperature. The dry sulphates are agitated with plenty of water, and filtered from a little insoluble residue of metallic acids. Ammonia in excess is then added to the filtrate, and the precipitated oxides are washed, once more converted into oxalates in the manner already described, and the oxalates again washed, dried, and ignited. The ignited oxides are boiled in dilute nitric acid, filtered from a little insoluble matter, and evaporated to dryness. These somewhat complicated operations are to insure the removal of sulphuric and metallic acids, the presence of which interferes with subsequent fractionation.

The earthy nitrates rich in scandium are mixed with an equal bulk of potassium nitrate and fused in large porcelain crucibles with constant stirring until the mass has the appearance of cream—fluid when hot, solidifying on cooling to a white enamel-like mass. On boiling this mass in water, a dense white basic nitrate separates and undecomposed nitrates are left in solution. Scandium and ytterbium, forming easily decomposed nitrates, concentrate in the insoluble end—the "heads,"—while the yttrium and cerium earths, whose nitrates are less easily decomposed by heat, are left in the soluble end—the "tails." Fractionation on these lines must now be continued until spectrum photographs show the scandium to be pure. It is not difficult to obtain scandia free from all earths present except ytterbia and yttria; but the final elimination of pure scandia from these earths is a matter demanding much time and patience.

This easy decomposition of the nitrate by heat makes it possible by a systematic series of fractionations to separate scandium from most of the other associated elements. The worst impurity is ytterbium, the nitrate of which is almost as easily decomposed. Fortunately a strong dominant line of the ytterbium spectrum, wave-length 3694·344, occurs at a vacant part of the scandium spectrum, and near the characteristic group of scandium. A sample of scandia is not considered satisfactory if the least trace of this line is seen on an over-exposed spectrum of scandium, and if the atomic weight is higher than 44·1. The atomic weight of ytterbium being 173, a very little of it as an impurity raises the atomic weight of scandium.

SCANDIUM HYDROXIDE,

$Sc_2O_3,3H_2O = Sc(OH)_3$.

On adding caustic alkali to a solution of a scandium salt the hydroxide comes down as a bulky gelatinous precipitate. It is insoluble in excess of precipitant. In appearance it resembles yttrium hydroxide. It dries in the air at ordinary temperatures to a hard porcelain-like mass and has the composition given above.

Analysis.

5·289 grs. lost on ignition 1·533 grs. of water.

	Theory.		Experiment.
Sc_2O_3	136·200	71·59	71·02
$3H_2O$	54·048	28·41	28·98
	190·248	100·00	100·00

The hydroxide is a very weak base, with a marked tendency to form basic salts. It dissolves readily in dilute acids, forming salts which have a sweet astringent taste. The salts show no absorption spectra.

After ignition, anhydrous scandia, Sc_2O_3, is difficultly soluble in dilute acids in the cold, rather more easily soluble when warmed, and readily soluble in hot strong mineral acids. Strong sulphuric acid poured on ignited scandia attacks it with considerable evolution of heat.

SCANDIUM CARBONATE,

$Sc_2(CO_3)_3,12H_2O$,

comes down as a bulky white precipitate on adding ammonium or sodium carbonate to a soluble salt of scandium. It is almost insoluble in a cold dilute solution of ammonium carbonate, but is moderately soluble in a hot and strong solution of this salt, and as in the same circumstances yttrium carbonate is much less soluble, this difference may be utilised as a basis for a method of separating scandium and yttrium by fractionation.

Scandium carbonate holds carbonic acid very weakly, and concordant analyses are not easy to get. Drying at 100° drives off water and some of the carbon dioxide, leaving a basic carbonate. When freshly precipitated and dried in a current of air at the ordinary temperature, the following formula best agrees with the figures obtained :—

$$Sc_2(CO_3)_3,12H_2O.$$

At a temperature of 100° this salt loses carbon dioxide and water, and becomes a basic salt of uncertain composition.

Strong ignition drives off all water and carbon dioxide, leaving Sc_2O_3.

HYDRATED SCANDIUM CHLORIDE,

$Sc_2Cl_6,12H_2O$.

The hydrated salt is prepared by dissolving the earth in hydrochloric acid and evaporating on a water-bath. It crystallises from a strong solution as a felt-like mass of fine white needles. The crystals should be pressed many times between filter-paper frequently renewed, and put to dry for a few hours in a desiccator over sulphuric acid. They are somewhat deliquescent, but not so much so as the nitrate, and are readily soluble in alcohol. They have the following composition :—

$$Sc_2Cl_6,12H_2O = Sc_2O_3,6HCl,9H_2O.$$

Analysis.

(1) 6·087 grs. of the pressed chloride left on ignition 1·620 grs. of scandia.

(2) 5·960 grs. of the pressed chloride lost 1·836 grs. after remaining in the water-oven at 100° for six hours.

	Theory.		Experiment.
			(1) and (2).
Sc_2O_3	136·200	26·34	26·61
6HCl	218·748	42·30	42·58
$9H_2O$	162·144	31·36	30·81
	517·092	100·00	100·00

When heated for six hours to a temperature of 100°, the 9 molecules of water go off, leaving a clear, colourless, and oily liquid, which on cooling solidifies to a white crystalline mass of the composition

$$Sc_2Cl_6,3H_2O = Sc_2O_3,6HCl.$$

When this salt is gradually heated to redness it gives off 6 molecules of hydrochloric acid with much intumescence, leaving a bulky residue of scandia.

Analysis.

(1) 4·235 grs. on ignition left 1·620 grs. of scandia, = 1·049 grs. of scandium.

(2) 4·124 grs. were dissolved in water and the scandia precipitated by ammonia. The scandia obtained weighed 1·592 grs., = 1·031 grs. of scandium.

	Theory.		Experiment.	
			(1).	(2).
2Sc. . . .	88·200	24·85	24·77	25·00
6Cl. . . . $3H_2O$ . . .	266·748	75·15	75·23	75·00
	354·948	100·00	100·00	100·00

Hydrated Scandium Bromide,

$Sc_2Br_6,12H_2O$.

Scandium hydroxide or carbonate dissolves easily in hydrobromic acid, and the acid solution evaporated on the water-bath deposits small rhombic crystals, coloured slightly brown by free bromine and very deliquescent. These crystals were collected on filter-paper and dried by pressure between folds of paper frequently renewed. They were then put into a silica weighing bottle, and dried in a desiccator over sulphuric acid.

Analysis.

(1) 29·753 grs. of the hydrated bromide gave on ignition 5·068 grs. of scandia.

(2) 29·753 grs. of the hydrated bromide lost at 120° 6·207 grs. of water.

	Theory.		Experiment.
			(1) and (2).
Sc_2O_3	136·200	17·37	17·03
6HBr	485·808	61·95	62·11
$9H_2O$	162·144	20·68	20·86
	784·152	100·00	100·00

When the hydrated bromide is heated in an air-bath to 120° it loses 9 molecules of water and becomes

$$Sc_2Br_6,3H_2O = Sc_2O_3,6HBr.$$

Analysis.

23·546 grs. of the dried bromide left on ignition 5·068 grs. of scandia.

	Theory.		Experiment.
Sc_2O_3	136·200	21·89	21·53
6HBr	485·808	78·11	78·47
	622·008	100·00	100·00

SCANDIUM FLUORIDE,

Sc_2F_6.

Ignited scandia is attacked by aqueous hydrofluoric acid, forming a semi-transparent gum-like mass, which on boiling changes to a fine white precipitate. This is difficult to filter, as it has great tendency to run through.

When hydrofluoric acid is added to a solution of scandium nitrate or sulphate, a white precipitate comes down. On boiling it becomes milky, resembling the above-described precipitate.

The fluoride dried over sulphuric acid is anhydrous. It slightly loses weight at a red heat, and at a yellow heat it frits together, fusing with difficulty before the blowpipe.

Strong sulphuric acid imperfectly decomposes scandium fluoride. It is completely decomposed by fusion with potassium bisulphate; the melt dissolves in acidulated water, and the solution mixed with ammonia deposits scandium hydroxide.

Analysis.

8·955 grs. of scandium fluoride, decomposed by fusion with potassium bisulphate and precipitated by ammonia, gave 6·0365 grs. of scandia, = 3·9091 grs. of scandium.

	Theory.		Experiment.
Sc_2	88·2	43·62	43·65
F_6	114·0	56·38	56·35
	202·2	100·00	100·00

SCANDIUM CHLORATE.

Aqueous chloric acid saturated with scandium hydroxide forms at first a clear colourless liquid; evaporation on the water-bath decomposes it, with evolution of chlorine. On further evaporation, crystals like long needles form on cooling, and the mother-liquor becomes a gummy amorphous mass in which, after standing, appear long needle-shaped crystals. These crystals probably are the perchlorate.

SCANDIUM PERCHLORATE.

Aqueous perchloric acid easily dissolves scandium hydroxide or carbonate, and the solution evaporated over the water-bath separates into a felt-like mass of rhombic needle-shaped crystals.

Scandium Bromate.

Bromic acid readily dissolves scandium hydroxide, but on evaporating the solution it decomposes, leaving an amorphous gummy mass without crystalline appearance.

Scandium Sulphate,

$Sc_2(SO_4)_3,6H_2O$.

Scandium hydroxide easily dissolves in dilute sulphuric acid; after ignition the oxide dissolves with difficulty in dilute, but readily in strong acid, with evolution of heat. The excess of sulphuric acid must be driven off carefully, when the anhydrous sulphate is left behind in the form of a fine white powder.

Nilson gives the formula of the anhydrous salt, $Sc_2O_6,3SO_2$. He says: "It loses acid at a high temperature, and leaves pure scandia. The salt treated with water only gives at first a milky liquid, the anhydrous salt combines very slowly with water, and then re-dissolves. On heating, a clear solution is immediately obtained." According to Cleve, "Sulphuric acid gives with scandia a white and bulky mass of sulphate, resembling thorium sulphate when it separates by heat. The sulphate does not form distinct crystals." It is very soluble in water, and a strong solution when heated does not deposit crystals, in that respect differing from most of the other rare-earth sulphates. The solution may be evaporated to a super-saturated syrup, which, standing in the cold for some hours, deposits crystals of the 6-hydrate. 100 parts of the saturated solution at 12° were found to contain 44·5 parts of anhydrous scandium sulphate. Scandium sulphate is not deliquescent in the ordinary air of a room even in damp weather, and is insoluble in alcohol. On mixing 100 grs. of anhydrous scandium sulphate with the same quantity of water, the temperature rose in a few minutes from 14° to 21°.

On adding absolute alcohol to a strong solution of scandium sulphate the solution becomes milky, and a heavy oily-looking liquid sinks to the bottom. This may be separated by filtration through paper moistened with alcohol, when the residue is left as a viscous liquid which on exposure to the air becomes thicker. This oily-looking liquid has the composition of the 6-hydrate sulphate.

When strongly heated, the sulphate decomposes, leaving pure scandia. It is, however, difficult to drive off all the sulphuric acid from the sulphate even by heating the crucible containing it before the blowpipe. The best way to decompose scandium sulphate is first to ignite it to the highest temperature of a Bunsen burner, then to moisten with water and add a little ammonium carbonate. Dry and ignite again, and pure scandia is left free from sulphuric acid.

Nilson says: "This salt separates from a syrupy solution in small globular aggregates. It is inalterable in the air, it loses four molecules of water at 100°, and the rest at a higher temperature." He found on analysis 14·26, 14·46, and 7·16, 7·29 of H_2O, instead of 14·88 and 7·44.

I have crystallised this sulphate from a syrupy aqueous solution; it is dried by repeated pressure between many folds of blotting-paper.

Analysis.

(1) 18·156 grs. of the crystallised 6-hydrate, finely powdered, and heated to 100° for three hours, lost 2·602 grs. of water, leaving a 2-hydrated sulphate.

(2) 20·725 grs., kept in a desiccator over sulphuric acid for 170 hours, lost 1·561 grs. of water, leaving a 4-hydrated sulphate.

(3) 29·138 grs. left on ignition 8·068 grs. of scandia.

(4) 31·508 grs. of the liquid sulphate, precipitated from solution on adding alcohol containing a little ether, were dissolved in water, and the scandia precipitated by ammonia. When dried and ignited it weighed 8·624 grs.

	Theory.		Experiment.
			(1), (2), (3), and (4).
Sc_2O_3	136·200	28·11	27·53
$3SO_3$	240·180	49·58	50·61
$2H_2O$	36·032	7·44	7·53
$4H_2O$	72·064	14·87	14·33
	484·476	100·00	100·00

The 6-hydrate effloresces in a dry atmosphere, and loses one molecule of water, becoming the 5-hydrate, which appears to be the most stable hydrate at ordinary temperatures:—

$$Sc_2(SO_4)_3,5H_2O.$$

Analysis.

(1). 16·619 grs. of the 5-hydrate, heated to 150°, lost 3·206 grs. of water.

(2) 16·619 grs., after drying as described and igniting to a yellow heat, left 4·878 grs. of scandia.

(3) 15·608 grs. of the 5-hydrate, heated *in vacuo* at 100° for twenty hours, and then for ninety minutes at 150°, lost 3·153 grs. of water. Ignited to a full yellow heat, it left 4·558 grs. of scandia.

(4) 38·819 grs., heated to just below visible redness, lost 8·019 grs. of water. (At this temperature a trace of basic sulphate is formed. This accounts for the excess over the theoretical loss of water.)

	Theory.		Experiment.				Mean.
			(1).	(2).	(3).	(4).	
Sc_2O_3 . . .	136·20	29·20	—	29·35	29·20	—	29·27
$3SO_3$ . . .	240·18	51·49	—	—	—	—	50·68
$5H_2O$ . . .	90·08	19·31	19·29	—	20·20	20·66	20·05
	466·46	100·00					100·00

Anhydrous Scandium Sulphate,

$Sc_2(SO_4)_3$.

When the hydrated sulphate is heated to 250° it loses the whole of the water and becomes anhydrous. Its composition now is $Sc_2(SO_4)_3$.

At a bright yellow heat all the sulphuric acid goes off.

Analysis.

(1) 30·716 grs. left on ignition 11·092 grs. of scandia.
(2) 18·907 grs. left on ignition 6·827 grs. of scandia.

Synthesis.

(3) 6·817 grs. of ignited scandia, converted into sulphate, yielded 18·907 grs. of scandium sulphate.

	Theory.		Experiment.		
			(1).	(2).	(3).
Sc_2O_3 . . .	136·20	36·19	36·11	36·11	36·06
$3SO_3$ . . .	240·18	63·81	63·89	63·89	63·94
	376·38	100·00	100·00	100·00	100·00

When the anhydrous sulphate is heated to dull redness it loses one molecule of SO_3, and becomes a basic salt of the composition

$$Sc_2O(SO_4)_2.$$

Synthesis.

4·622 grs. of ignited scandia were dissolved in strong sulphuric acid, the excess of acid driven off by heat, and the dry sulphate heated to dull redness. It weighed 10·121 grs.

	Theory.		Experiment.
Sc_2O_3	136·20	45·97	45·67
$2SO_3$	160·12	54·03	54·33
	296·32	100·00	100·00

SCANDIUM AND POTASSIUM DOUBLE SULPHATE,

$3K_2SO_4,Sc_2(SO_4)_3$.

The behaviour of the double sulphates of potassium and the rare-earth metals is usually considered to govern their position in the broad groups into which they are divided. If the double sulphate is insoluble in a saturated solution of potassium sulphate the earth is supposed to belong to the cerium group, while if the double sulphate is soluble the earth is said to be one of the yttrium group. According to CLEVE ('Comptes Rendus,' vol. lxxxix., p. 419, August 18, 1879):—"Potassium sulphate in concentrated solution gives rise to the separation of a double salt, a crystalline powder, soluble in a saturated solution of potassium sulphate." CLEVE gives the composition of the double salt as $Sc_2O_3,3SO_3+2K_2O,SO_3$. On the other hand, NILSON says ('Comptes Rendus,' vol. xci., p. 118, July 12, 1880):—"Scandium sulphate in a saturated solution of potassium sulphate gives a double salt, completely insoluble. . . . It dissolves with difficulty in water, even boiling, and not at all in a saturated solution of potassium sulphate. . . . The composition of the double salt, $3K_2O_2SO_2+Sc_2O_63SO_2$, shows that scandium belongs to the group of gadolinite and cerite metals, all these metals giving salts of the same typical composition."

In view of these diametrically opposite statements I have taken especial pains to ascertain the true behaviour of the double salt.

17·717 grs. of re-crystallised scandium sulphate, found by analysis to be pure, were dissolved in water in a flask. The calculated quantity of potassium sulphate to unite with the 17·717 grs., and to make a saturated solution in the water added, was then weighed out, and 5 per cent. additional potassium sulphate was added to ensure complete saturation. This was dissolved in boiling water, put into the flask containing the scandium sulphate, and water up to 250 cc. was added. The flask was securely corked, and put into a mechanical agitator, where it was shaken continuously for twenty-five hours. At first, when the two salts were mixed, no precipitation of double salt was visible, but after a short time there appeared a fine granular precipitate, which gradually increased as the shaking proceeded.

At the end of twenty-five hours the precipitated double sulphate was filtered off and washed with 100 cc. of cold saturated solution of potassium sulphate. The filtrate was heated, ammonia added, and the whole well boiled. A very slight precipitate of scandia came down which, when filtered, washed, and ignited, weighed 0·414 gr., equivalent to 1·473 grs. of scandium sulphate in solution, the rest of the sulphate being in the insoluble precipitate. It therefore follows that for every 100 parts of the double sulphate 8·32 per cent. are soluble and 91·68 per cent. are insoluble in the amount of saturated solution of potassium sulphate employed.

The insoluble double salt was washed with boiling water to remove the little excess of potassium sulphate, until its bulk was reduced about one-half. It was then dried and analysed.

My own analytical results agree closely with NILSON'S formula. As CLEVE distinctly says that the double sulphate is soluble in a saturated solution of potassium sulphate, it is probable he was not working on the true double salt.

The scandia in the aqueous washings was also determined. The total amount of scandia in the washings and precipitate amounted to 4·560 grs., which, added to the 0·414 in the solution, makes 4·974 grs. of scandia. The 17·717 grs. of scandium sulphate contain theoretically 4·981 grs. of scandia, so these results are well within experimental errors.

SCANDIUM SELENATE,

$$Sc_2(SeO_4)_3,8H_2O.$$

Dilute and warm selenic acid easily dissolves scandium hydrate or carbonate, and on evaporating the acid solution over sulphuric acid the selenate crystallises in well-defined rhombic prisms, bright, colourless, and capable of withstanding a temperature of 400° without decomposition, except loss of water.

When heated to 100° for sixteen hours, the 8-hydrate loses 6 molecules of water and becomes a 2-hydrate,

$$Sc_2(SeO_4)_3,2H_2O.$$

Analysis.

(1) 16·847 grs. of crystallised scandium selenate, heated to 400°, lost 3·709 grs. of water.

(2) 16·847 grs. of the same salt gave on ignition to a full yellow heat 3·485 grs. of scandia, = 2·257 grs. of scandium.

(3) 13·913 grs. of the crystallised salt, heated to 100° for sixteen hours, lost 2·293 grs. of water.

	Theory.			Experiment.	
				(1), (2).	(3).
Sc_2	88·200	13·33		13·39	—
$3SeO_4$ . . .	429·600	64·90		64·60	—
$6H_2O$ . . .	108·096	16·33	21·77	22·01	16·48
$2H_2O$ . . .	36·032	5·44			—
	661·928	100·00		100·00	

The anhydrous selenate, heated to a full yellow heat, loses all the selenic acid, and scandia remains.

Analysis.

13·138 grs. of anhydrous selenate left 3·485 grs. of scandia, = 2·257 grs. of scandium.

	Theory.		Experiment.
Sc_2	88·2	17·03	17·18
$3SeO_4$ . . .	429·6	82·97	82·82
	517·8	100·00	100·00

SCANDIUM NITRATE,

$Sc(NO_3)_3,4H_2O$.

When hydrated, scandia easily dissolves in dilute nitric acid; after ignition it dissolves with the aid of heat in moderately strong nitric acid. The salt is very soluble in water and in alcohol, and is extremely deliquescent. The acid solution, over sulphuric acid, dries up to a viscous gummy mass, in which appear groups of stellate crystals. A neutral aqueous solution evaporated on the water-bath, on cooling, deposits colourless prismatic crystals.

Scandium nitrate decomposes more easily by heat than the nitrate of any other of the rare earths. The crystals deposited from an almost neutral solution get pasty at 100°, but do not run to liquid. In vacuum at 100° the crystals give off water, and frit together, but do not become liquid. Dried on a water-bath, and heated in a tube immersed in melted paraffin with a thermometer by its side, they show signs of melting at 125°. They commence to liquefy at 150°, and when stirred with a platinum wire the crystals run together and form an opaque white liquid.

When scandium nitrate is partly decomposed by heat, and the melted mass extracted with hot water and well boiled, a basic nitrate then deposits, which is difficult to filter owing to its clogging fineness.

The hydrated nitrate, gradually heated in a silica crucible, fuses and boils, becomes opaque and evolves much water. If the heating is stopped at the proper time, the anhydrous nitrate is left, the whole of the water having been driven off. On continuing the heat nitrous vapours come off and the liquid becomes clear and liquid like water. Increasing the heat turns the liquid brown and drives off more nitrous vapours, ebullition becomes sluggish, the fused mass gets white and opaque, and finally there remains a white residue of scandia.

For analysis the nitrate was thrice re-crystallised and repeatedly dried between blotting-paper.

Analysis.

(1) 11·136 grs., gradually heated to full redness, left 2·537 grs. of scandia, = 1·6429 grs. of scandium.

(2) 25·978 grs. left 5·914 grs. of scandia, = 3·8297 grs. of scandium.

	Theory.		Experiment.	
			(1).	(2).
Sc	44·100	14·59	14·75	14·74
$3(NO_3)$ . . . $4H_2O$	258·094	85·41	85·25	85·26
	302·194	100·00	100·00	100·00

When the above hydrate is dried over a water-bath, it does not fuse, but becomes pasty and anhydrous—

$$Sc(NO_3)_3.$$

Analysis.

(1) 38·795 grs. left on ignition 11·449 grs. of scandia, = 7·4141 grs. of scandium.

(2) 11·026 grs. of nitrate left on ignition 3·233 grs. of scandia, = 2·0936 grs. of scandium.

(3) 14·618 grs. of nitrate left on ignition 4·287 grs. of scandia, = 2·7762 grs. of scandium.

Synthesis.

(4) 4·246 grs. of ignited scandia (= 2·7496 grs. of scandium) were covered in a crucible with strong nitric acid and put into a hot oven at 100° for seven hours. All excess of nitric acid disappeared, and a clear oily liquid remained which solidified on cooling. No crystals were seen, but the substance resembled glass. The solid nitrate weighed 14·008 grs.

(5) 3·233 grs. of scandia (= 2·0936 grs. of scandium), treated as described in the last experiment, formed 11·026 grs. of nitrate.

	Theory.		Experiment.				
			(1).	(2).	(3).	(4).	(5).
Sc . .	44·10	19·16	19·11	18·99	18·99	19·63	18·99
$3(NO_3)$.	186·03	80·84	80·89	81·01	81·01	80·37	81·01
	230·13	100·00	100·00	100·00	100·00	100·00	100·00

When the hydrated nitrate is dried *in vacuo* at 100° for seventeen hours it becomes a basic nitrate

$$ScOH(NO_3)_2,H_2O.$$

Analysis.

21·679 grs. of this basic nitrate lost on ignition 14·475 grs., and left 7·204 grs. of scandia, = 4·665 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	21·71	21·52
OH . . . . . $(NO_3)_2$ . . . . H_2O	159·044	78·29	78·48
	203·144	100·00	100·00

Therefore the nitrate has lost one equivalent of nitric acid.

When the nitrate is heated for twelve hours in a hot-air oven at a temperature of 120°, a basic nitrate is left of the composition

$$Sc_2O(NO_3)_4.$$

Analysis.

(1) 6·550 grs. left on ignition 2·537 grs. of scandia, = 1·6429 grs. of scandium.
(2) 13·698 grs. left on ignition 5·287 grs. of scandia, = 3·4237 grs. of scandium.

	Theory.		Experiment.	
			(1).	(2).
2Sc	88·20	25·04	25·08	24·99
O . . . . . . $4(NO_3)$ . . .	264·04	74·96	74·92	75·01
	352·24	100·00	100·00	100·00

SCANDIUM FORMATE,

$(HCOO)_2ScOH,H_2O$.

Scandium hydroxide dissolves readily in formic acid. The solution is evaporated to expel excess of acid and dissolved in water. It is then allowed to evaporate over sulphuric acid in a desiccator, when it forms hard and lustrous crystals, easily soluble in hot water and in alcohol.

The formate readily decomposes when heated, and at a red heat leaves a white residue of scandia.

Analysis.

8·895 grs. of crystallised formate left on ignition 3·650 grs. of scandia, = 2·363 grs. of scandium.

	Theory.		Experiment.
Sc	44·10	26·07	26·57
$(HCOO)_2$ OH H_2O	125·04	73·93	73·43
	169·14	100·00	100·00

Scandium Acetate,

$(CH_3COO)_2ScOH,2H_2O$.

Scandium oxide after ignition does not dissolve in acetic acid. The hydroxide, however, dissolves easily, and the acetate soon separates from the liquid in the form of fine white crystals, difficultly soluble in water. The aqueous solution, evaporated over the water-bath, deposits hard crystalline crusts.

When freshly prepared, the acetate dried in the air has the composition given below. Water, however, is slowly given off, and after standing some days the salt passes into a monohydrate analogous to the formate.

When ignited, the acetate leaves a grey residue of scandia containing carbon. By ignition alone it is difficult to get it of a constant weight. The best way to analyse the salt is to moisten the weighed acetate with a few drops of nitric acid and cautiously to evaporate to dryness, heat, and ignite. In this way is obtained pure white scandia.

Analysis.

(1) 7·795 grs. of acetate left 2·449 grs. of scandia, = 1·5859 grs. of scandium.
(2) 7·133 grs. left 2·270 grs. of scandia, = 1·4697 grs. of scandium.
(3) 19·035 grs. left on ignition 6·000 grs. of scandia, = 3·8848 grs. of scandium.

	Theory.		Experiment.		
			(1).	(2).	(3).
Sc	44·100	20·49	20·35	20·60	20·41
$(CH_3COO)_2$ OH $2H_2O$	171·088	79·51	79·65	79·40	79·59
	215·188	100·00	100·00	100·00	100·00

After being exposed to dry air for several days, the dihydrate loses one molecule of water of crystallisation, and becomes a monohydrate—

$(CH_3COO)_2ScOH,H_2O$.

Analysis.

14·690 grs. left 5·262 grs. of scandia, = 3·4075 grs. of scandium.

	Theory.		Experiment.
Sc . . .	44·100	22·37	23·19
$(CH_3COO)_2$ . . OH . . . . . H_2O	153·072	77·63	76·81
	197·172	100·00	100·00

SCANDIUM PROPIONATE,

$(C_2H_5COO)_2ScOH$.

Propionic acid readily attacks scandium hydroxide, forming a difficultly soluble white amorphous salt. On evaporating the excess of acid the scandium propionate is left as a voluminous white powder. 100 parts of cold water dissolve 1·23 parts of scandium propionate, the greater part being precipitated on heating the solution, and re-dissolved on cooling. When boiled in water, the salt floats greasily about the surface. The propionate is easily soluble in alcohol even in the cold, and when the alcoholic solution is allowed to evaporate the propionate is deposited as a mass of minute spherical concretions with no appearance under the microscope of crystalline structure.

The scandium propionate so obtained has the formula

$$(C_2H_5COO)_2ScOH.$$

Analysis.

15·978 grs. on ignition yielded 5·287 grs. of scandia, = 3·424 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	21·29	21·43
OH . . . . . $(C_2H_5COO)_2$ . .	163·088	78·71	78·57
	207·188	100·00	100·00

SCANDIUM BUTYRATE,

$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COO)_2ScOH.$$

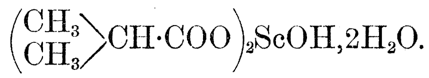
When scandium hydroxide is heated with butyric acid, a white amorphous and difficultly soluble salt is produced. When boiled in water, the butyrate softens to a plastic mass, becoming hard and brittle on cooling. Like other scandium salts of the fatty acids, scandium butyrate is more soluble in cold than in hot water, and is precipitated from a cold solution on boiling. It is easily soluble in alcohol. The solution in cold water, evaporated over a water-bath, leaves a residue which under the microscope is seen to consist of minute spherical groups, radiating from a central nucleus.

Analysis.

6·251 grs. of butyrate yielded on ignition 1·826 grs. of scandia, = 1·182 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	18·75	18·91
OH . . . . . $2(C_3H_7COO)$ . .	191·120	81·25	81·09
	235·220	100·00	100·00

SCANDIUM ISO-BUTYRATE,



$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{\cdot}COO\right)_2ScOH,2H_2O.$$

This salt is prepared in a similar manner to the butyrate, which it much resembles in appearance. It is more soluble in cold than in hot water, a saturated cold solution becoming thick and depositing amorphous flakes when heated. On cooling the liquid becomes clear again; in this respect it closely resembles calcium butyrate. It is very soluble in alcohol and is precipitated by water from the alcoholic solution.

The formula of the iso-butyrate differs from that of the butyrate in having two molecules of water of crystallisation :—

$$(C_3H_7COO)_2ScOH,2H_2O.$$

Analysis.

9·994 grs. of scandium iso-butyrate gave on ignition 2·550 grs. of scandia, = 1·651 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	16·26	16·52
OH	227·152	83·74	83·48
$2(C_3H_7COO)$ . .			
$2H_2O$			
	271·252	100·00	100·00

SCANDIUM ISO-VALERATE,

$(C_4H_9COO)_2ScOH,2H_2O$.

Scandium hydroxide is readily attacked by aqueous iso-valeric acid, forming a white amorphous salt, soluble in cold water, precipitated on boiling, and again dissolved on cooling. Dried over sulphuric acid the iso-valerate has the composition

$$(C_4H_9COO)_2Sc(OH),2H_2O.$$

Analysis.

10·902 grs. of scandium iso-valerate left on ignition 2·493 grs. of scandia, = 1·614 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	14·74	14·80
OH	255·184	85·26	85·20
$2(C_4H_9COO)$ . .			
$2H_2O$			
	299·284	100·00	100·00

SCANDIUM OXALATE,

$Sc_2(C_2O_4)_3,5H_2O$.

Scandium oxalate comes down as a white crystalline powder when oxalic acid or ammonium oxalate is added to a solution of scandium. If much free mineral acid is present the precipitation is not immediate; it begins by a cloudiness, which in a few minutes increases to a crystalline precipitate, a little scandium oxalate remaining in the solution. It is slightly soluble in water, weak acids, and more so in solution of ammonium oxalate. On boiling a mixed oxalate from wiikite in a solution of ammonium oxalate the portion dissolved was richer in scandium than the insoluble part. Attempts were made to effect a separation of scandia from the accompanying earths by making use of this fact. A mixed oxalate of crude earths was boiled in a strong solution of ammonium oxalate and then filtered, and this operation was repeated on the residue several times. Ultimately the most soluble and the least soluble earths were separated and their spectra photographed. The most soluble earth was nearly all scandia, with a little yttria, and traces of ytterbia, titania, and lime. The least soluble contained more yttria than scandia, but not much of either. By a repetition of this process it would not be difficult to effect a good separation of scandia and yttria; I think the fused nitrate process is simpler and quicker.

When crude scandium oxalate is boiled in a solution of ammonium oxalate a partial separation of the earths is effected, but it is less complete than when ammonium carbonate is used as a solvent. This is a very good method for separating scandia from zirconia, as hardly a trace of the zirconia is to be seen in the portion insoluble in hot ammonium oxalate.

According to NILSON ('Comptes Rendus,' vol. xci., p. 121), the precipitated oxalate is slightly soluble in weak acids, and even in water. I have verified this observation; care must be taken not to over-wash the oxalate, or loss will ensue, and the filtrates should be kept and worked again for scandium.

The precipitated oxalate, dried in the air, contains 5 molecules of water.

Analysis.

(1) 22·445 grs., ignited at a yellow heat, left 6·988 grs. of scandia.
(2) 21·873 grs. ignited left 6·806 grs. of scandia.

	Theory.		Experiment.	
			(1).	(2).
Sc_2O_3 . . .	136·20	30·79	31·13	31·12
$3C_2O_3$ . . . $5H_2O$ . . .	306·08	69·21	68·87	68·88
	442·28	100·00	100·00	100·00

When the 5-hydrated oxalate is allowed to dry at the ordinary temperature over sulphuric acid, it loses 2 molecules of water and becomes a 3-hydrate

$$Sc_2(C_2O_4)_3,3H_2O.$$

Analysis.

7·639 grs. left on ignition at a yellow heat 2·529 grs. of scandia.

	Theory.		Experiment.
Sc_2O_3	136·200	33·53	33·11
$3C_2O_3$ . . . . $3H_2O$	270·048	66·47	66·89
	406·248	100·00	100·00

The 5-hydrate of scandium oxalate, dried in a hot-air oven at 100°, loses 3 molecules of water and becomes a 2-hydrate

$$Sc_2(C_2O_4)_3,2H_2O.$$

Analysis.

22·445 grs. lost 2·014 grs. of water.

	Theory.		Experiment.
Sc_2O_3 $3C_2O_3$	352·200	90·72	91·03
$2H_2O$	36·032	9·28	8·97
	388·232	100·00	100·00

The hydrated oxalate, dried *in vacuo* at 100° or in air at 140°, loses all but one molecule of water and becomes a mono-hydrate

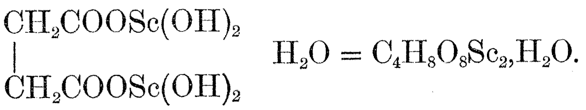
$$Sc_2(C_2O_4)_3,H_2O.$$

Analysis.

(1) 32·118 grs. left on ignition 11·756 grs. of scandia.
(2) 15·694 grs. left 5·815 grs. of scandia.
(3) 8·304 grs. left 3·010 grs. of scandia.

	Theory.		Experiment.		
			(1).	(2).	(3).
Sc_2O_3	136·200	36·79	36·60	37·05	36·25
$3C_2O_3$ H_2O	234·016	63·21	63·40	62·95	63·75
	370·216	100·00	100·00	100·00	100·00

SCANDIUM SUCCINATE,



$$\begin{array}{l} CH_2COOSc(OH)_2 \\ | \\ CH_2COOSc(OH)_2 \end{array} \quad H_2O = C_4H_8O_8Sc_2,H_2O.$$

This salt comes down as an insoluble white precipitate when dilute solutions of ammonium succinate and scandium nitrate are mixed. It also may be prepared by boiling scandium hydroxide in solution of succinic acid. It is slightly soluble in excess of either reagent, and is insoluble in water or alcohol. When dried in the air it forms a hard porcelain-like mass.

Analysis.

12·713 grs. of scandium succinate heated for ten hours to 180° lost 0·822 gr. of water, and when ignited to full redness it left 6·089 grs. of scandia, = 3·9431 grs. of scandium.

	Theory.			Experiment.
Sc_2	88·200		30·38	31·02
C_4	48·000	184·064	63·41	62·51
H_8	8·064			
O_8	128·000			
H_2O	18·016		6·21	6·47
	290·280		100·00	100·00

SCANDIUM PICRATE,

$$\{C_6H_2(NO_2)_3O\}_2ScOH,14H_2O.$$

The hydroxide dissolves readily in warm solution of picric acid and separates in groups of long needle-shaped crystals of a rich yellow colour. When rapidly crystallised from a strong solution, the crystals form confused feathery masses, which on pouring off the mother-liquor turn to a felt-like mass difficult to drain. 100 parts of water at 20° dissolve 0·95 part of scandium picrate. At 9° the same quantity of water dissolves 0·37 part. Dried by exposure to cold dry air the crystals have the composition shown above.

The picrate cannot be detonated when wrapped in tin-foil and struck on an anvil with a heavy hammer. Heated in a dry test-tube it darkens, gives a slight sublimate, fuses, and at a little higher temperature faintly explodes, leaving a black flocculent residue, which burns off to pure white scandia at a red heat.

The explosion, although not violent, is sufficient to blow some of the products out of the crucible. The scandia therefore was estimated by precipitating the hot solution with ammonia in considerable excess and well boiling the liquid before filtering. Unless this precaution is taken some of the picrate precipitates as such, and slight explosions occur when the precipitate is burnt.

Analysis.

(1) 27·497 grs. of picrate, dried at 100°, gave off 5·906 grs. of water.

(2) 27·497 grs. yielded 2·422 grs. of scandia, = 1·569 grs. of scandium.

	Theory.		Experiment. (1) and (2).
Sc	44·100	5·73	5·71
OH . . . . . . $2\{C_6H_2(NO_2)_3O\}$. $5H_2O$	563·180	73·20	72·81
$9H_2O$	162·144	21·07	21·48
	769·424	100·00	100·00

When the 14-hydrate is heated to 100°, nine molecules of water go off, leaving a 5-hydrate

$$\{C_6H_2(NO_2)_3O\}_2,ScOH,5H_2O.$$

Analysis.

21·657 grs. of the picrate, dried at 100°, gave 2·422 grs. of scandia, = 1·569 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	7·26	7·24
OH . . . . . . $2\{C_6H_2(NO_2)_3O\}$. $5H_2O$	563·180	92·74	92·76
	607·280	100·00	100·00

SCANDIUM BENZOATE,

$$(C_6H_5COO)_3Sc.$$

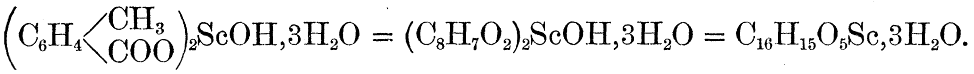
Scandium benzoate comes down as a white curdy precipitate on adding a solution of ammonium benzoate to scandium nitrate solution. On boiling the solution the precipitate collects as a crystalline powder. It is slightly soluble in water and alcohol, and easily soluble in dilute mineral acids.

Analysis.

12·303 grs. of scandium benzoate left on ignition 2·204 grs. of scandia, = 1·4272 grs. of scandium.

	Theory.			Experiment.
Sc	44·10		10·83	11·60
C_{21} . . . . H_{15} . . . . O_6	252·00 15·12 96·00	363·12	89·17	88·40
	407·22		100·00	100·00

SCANDIUM ORTHO-TOLUATE,



$$\left(C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COO\end{matrix}\right)_2ScOH,3H_2O = (C_8H_7O_2)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$$

When scandium hydroxide is boiled with an excess of aqueous ortho-toluic acid, a salt is formed with the composition given above. It is a white crystalline powder insoluble in water.

The same salt is formed by mixing solutions of ammonium ortho-toluate and scandium nitrate. It forms a voluminous white curdy precipitate, insoluble in hot or cold water. It contains 3 molecules of water, which are not driven off at 150°.

Analysis.

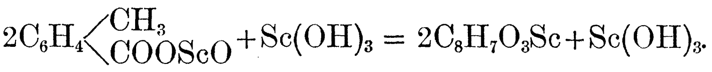
12·316 grs. of scandium ortho-toluate dried *in vacuo* over sulphuric acid left on ignition 2·171 grs. of scandia, = 1·4059 grs. of scandium.

		Theory.		Experiment.
Sc		44·100	11·45	11·42
C_{16}	192·000	341·168	88·55	88·58
H_{15}	15·120			
O_5	80·000			
$3H_2O$ . . .	54·048			
		385·268	100·00	100·00

It is seen that this ortho-toluate has the same percentage composition as the phenyl-acetate, but differs in structural constitution.

BASIC SCANDIUM ORTHO-TOLUATE.

When scandium hydroxide is boiled with solution of ortho-toluic acid, keeping the hydroxide in slight excess, a basic scandium ortho-toluate is formed. It can be decanted easily from the excess of hydroxide, which is of greater density; it is anhydrous and has the composition



$$2C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COOScO\end{matrix}+Sc(OH)_3 = 2C_8H_7O_3Sc+Sc(OH)_3.$$

This basic ortho-toluate is a white powder, insoluble in water and alcohol, but easily soluble in dilute acids.

Analysis.

(1) 6·402 grs. of basic scandium ortho-toluate, dried over sulphuric acid *in vacuo*, left on ignition 2·711 grs. of scandia, = 1·7556 grs. of scandium.

(2) 7·631 grs. of basic scandium ortho-toluate left on ignition 3·219 grs. of scandia, = 2·0846 grs. of scandium.

		Theory.		Experiment.	
				(1).	(2).
Sc_3 . . .		132·300	27·25	27·42	27·32
C_{16} . . .	192·000	353·136	72·75	72·58	72·68
H_{17} . . .	17·136				
O_9 . . .	144·000				
		485·436	100·00	100·00	100·00

The above basic salt is formed by the union of two molecules of the ortho-toluate, $C_8H_7O_3Sc$, with one molecule of scandium hydroxide, $Sc(OH)_3$.

Scandium Meta-toluate,

$$\left(\mathrm{C_6H_4}\!<\!\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COO}\end{array}\right)_2\mathrm{ScOH,3H_2O} = \mathrm{(C_8H_7O_2)_2ScOH,3H_2O} = \mathrm{C_{16}H_{15}O_5Sc,3H_2O}.$$

This salt is formed by double decomposition between ammonium meta-toluate and scandium nitrate solutions. It comes down as a voluminous white curdy precipitate, insoluble in water.

Analysis.

15·702 grs. of the meta-toluate, dried *in vacuo* over sulphuric acid at the ordinary temperature, left on ignition 2·673 grs. of scandia, = 1·7310 grs. of scandium.

		Theory.		Experiment.
Sc		44·100	11·45	11·02
C_{16}	192·000	341·168	88·55	88·98
H_{15}	15·120			
O_5	80·000			
$3H_2O$ . . .	54·048			
		385·268	100·00	100·00

Scandium Para-toluate,

$$\left(\mathrm{C_6H_4}\!<\!\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COO}\end{array}\right)_2\mathrm{ScOH,3H_2O} = \mathrm{(C_8H_7O_2)_2ScOH,3H_2O} = \mathrm{C_{16}H_{15}O_5Sc,3H_2O}.$$

Scandium para-toluate is formed by double decomposition in the same manner as the ortho-toluate, and has the same composition. It separates with three molecules of water, which are not driven off at 150°. It is a white curdy precipitate insoluble in hot or cold water.

Analysis.

12·332 grs. of scandium para-toluate on ignition left 2·141 grs. of scandia, = 1·3865 grs. of scandium.

		Theory.		Experiment.
Sc		44·100	11·45	11·24
C_{16}	192·000	341·168	88·55	88·76
H_{15}	15·120			
O_5	80·000			
$3H_2O$ . . .	54·048			
		385·268	100·00	100·00

Scandium Phenyl-acetate,

$$(C_6H_5CH_2COO)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$$

Scandium hydroxide is readily attacked by aqueous phenyl-acetic acid, with the formation of a white insoluble phenyl-acetate. The salt thus prepared has, however, a tendency to become more basic, and a better way to prepare it is by double decomposition between ammonium phenyl-acetate and scandium nitrate. When moderately dilute and hot solutions of these salts are mixed and the whole boiled, the phenyl-acetate comes down chiefly on the sides and bottom of the beaker, and adheres to the glass with great pertinacity. It can only be removed with difficulty and risk of breakage. The deposit on the glass looks like warty concretions and under a high power appears crystalline. It is almost insoluble in hot or cold water, and is insoluble in alcohol.

When double decomposition between scandium nitrate and ammonium phenyl-acetate is effected in the cold, the salt comes down as a white curdy precipitate which does not adhere to the glass, and can be washed easily with warm water; boiling water, however, causes it to cohere with contraction. The dry salt when heated softens and can be pressed into a pasty mass. It does not fuse at a temperature at which decomposition begins.

Analysis.

(1) 13·584 grs. of scandium phenyl-acetate precipitated from hot solutions and washed with boiling water, filtered and dried at 100° till the weight was constant, yielded on ignition 2·396 grs. of scandia, = 1·5516 grs. of scandium.

(2) 9·458 grs. of scandium phenyl-acetate precipitated from cold solutions, washed and dried at 100° to a constant weight, gave on ignition 1·671 grs. of scandia, = 1·0821 grs. of scandium.

	Theory.			Experiment.	
				(1).	(2).
Sc		44·100	11·45	11·42	11·44
C_{16}	192·000	341·168	88·55	88·58	88·56
H_{15}	15·120				
O_5	80·000				
$3H_2O$	54·048				
		385·268	100·00	100·00	100·00

Attempts to estimate the water were unsuccessful, as the phenyl-acetate turned brown and commenced to decompose when heated above 160°, at which temperature the whole of the three molecules of water were not expelled.

Scandium Pyromellitate,

$$C_6H_2\{COOSc(OH)_2\}_4 2H_2O = Sc_4C_{10}H_{10}O_{16}, 2H_2O.$$

This salt comes down when ammonium pyromellitate is added to a solution of a soluble scandium salt. It is formed also by allowing pyromellitic acid to act on scandium hydroxide with the aid of gentle heat. Scandium pyromellitate is a white amorphous powder, insoluble in water and alcohol, but soluble in dilute acids.

Of the two molecules of water of hydration one is driven off at 100° and the remaining molecule at 140°. The dried salt can be heated to 220° without decomposition.

Analysis.

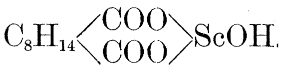
(1) 14·304 grs. of scandium pyromellitate dried at 140° for some hours lost 0·847 grs. of water; when ignited to full redness, treated with nitric acid, and ignited again, it left 6·515 grs. of scandia, = 4·2190 grs. of scandium.

(2) 11·485 grs. of scandium pyromellitate dried at 100° lost 0·350 gr. of water, and, when ignited as above, left 5·170 grs. of scandia, = 3·3480 grs. of scandium.

(3) 7·614 grs. of scandium pyromellitate heated to 220° for three hours lost 0·464 gr. of water, and, when ignited as already described, left 3·501 grs. of scandia, = 2·2672 grs. of scandium.

	Theory.			Experiment.		
				(1).	(2).	(3).
Sc_4	176·400	29·47		29·50	29·15	29·78
C_{10} H_{10} O_{16}	386·080	64·51		64·58	64·83	64·13
H_2O	18·016	3·01	6·02	5·92	3·05	6·09
H_2O	18·016	3·01			2·97	
	598·512	100·00		100·00	100·00	100·00

Scandium Camphorate,



$$C_8H_{14}\left<\begin{matrix}COO\\COO\end{matrix}\right>ScOH.$$

The camphorate is prepared by heating scandium hydroxide with a slight excess of camphoric acid and water. The hydroxide is easily attacked and converted into an insoluble camphorate. It may be prepared also by precipitating a solution of scandium nitrate with a solution of ammonium camphorate. In either case it forms an insoluble white precipitate, which, after thorough washing and drying at 100°, has the composition given above.

Scandium camphorate is anhydrous and insoluble in water and alcohol. It is easily soluble in dilute mineral acids. When dry it is very electrical, and an attempt to powder it sends it flying out of the mortar. If it is put warm between two watch-glasses, and the lower glass is gently rubbed on the outside with the finger, the path of the finger is marked by a flight of camphorate from the lower to the upper glass, where it sticks. This peculiarity makes it not easy to perform the preliminary operations of drying, transferring, and weighing, preparatory to its quantitative analysis.

Gradually heated to redness, the camphorate at first blackens with carbon. At a red heat this burns off, leaving a white residue of scandia.

Analysis.

(1) 18·191 grs. of the camphorate, dried at 100°, yielded on ignition 4·772 grs. of scandia, = 3·0902 grs. of scandium.

(2) 17·921 grs. of the camphorate yielded on ignition 4·719 grs. of scandia, = 3·0559 grs. of scandium.

		Theory.	Experiment.	
			(1).	(2).
Sc	44·10	17·01	16·99	17·05
C_{10}	120·00	82·99	83·01	82·95
H_{15}	15·12			
O_5	80·00			
	259·22	100·00	100·00	100·00

Added April 30th, 1908.

Scandium is remarkable inasmuch as its existence was foretold by MENDELEEFF,* and called by him ekaboron, eight years before its actual discovery by NILSON. To-day I may be permitted to indulge still further in speculations on the genesis and degradation of the chemical elements—speculations which a few years ago might have been derided even by a learned Society. But the undoubted fact of the production of helium from radium, the probability that chemical elements of high atomic weight are slowly breaking up into bodies of lower atomic weight, and the suspicion that some well-known chemical elements of low atomic weight are degradation products, embolden me to speculate on the past history and genesis of scandium.

In 1898 I brought before the Royal Society a scheme of the arrangement in Space of the chemical elements in which scandium was seen to fall in place between boron and yttrium. I hesitated to introduce ytterbium into the scheme, as its atomic weight was not known with sufficient accuracy to enable it to be properly placed. To-day it is seen to fill a gap below yttrium, and the group is:—Boron, scandium, yttrium, ytterbium. These four elements have a close relationship, thus:—

B	atomic weight	$11{\cdot}0 \times 16 = 176{\cdot}0$
Sc	,, ...	$44{\cdot}1 \times 4 = 176{\cdot}4$
Y	,, ...	$89{\cdot}0 \times 2 = 178{\cdot}0$
Yb	,, ...	$173{\cdot}0 \times 1 = 173{\cdot}0$

In reference to this table it must be remarked that the atomic weight of scandium certainly is not known with absolute accuracy, the ·1 being little more than a guess. Yttrium, moreover, is now seen to be very liable to contain scandium; when CLEVE determined its atomic weight it was impossible, without further refined spectroscopic examination—not available at that date—to detect in it the trace of scandium sufficient to lower the atomic weight by one unit. Ytterbium certainly is too low, for URBAIN recently has announced the discovery in it of an element of a lower atomic weight; this being removed might raise the atomic weight of ytterbium a few units. With these reasonable corrections the last column will not be far from the same whole number, 176.

The frequent occurrence of the triad ytterbium, yttrium, and scandium in a very limited group of rare minerals may be explained by assuming the instability of ytterbium, the atom of highest weight, and letting it split into two atoms, when yttrium would be produced. Assume the same action to take place with yttrium, its splitting up again into two atoms would produce scandium; and scandium ("*eka-boron*,

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* D. I. MENDELEEFF, "A Natural System of the Elements, and its Application to the Indication of the Properties of Undiscovered Elements," 'Russ. Chem. Soc. Journ.,' 1871, iii., pp. 25–56.

next in order to boron") would ultimately form boron by a quadruple sub-division. The comparatively small quantities of ytterbium and scandium in these minerals may easily be accounted for by the assumption that they are more unstable forms of matter than yttrium and boron.

The fact that these bodies give totally distinct line spectra has not the significance it formerly was supposed to have, for now we know of different line spectra given by the same body. Argon, with its red and blue spectra, is a case in point, and GOLDSTEIN, as a result of his work on the spectra of Cs, Rb, and K, has come to the conclusion that the property of emitting two separate line spectra is a general one. Moreover, between the line spectra of radium, uranium, and helium—bodies which are supposed to be associated genetically—there is no similarity or line in common.

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"Brilliant Spectral Rays of the Metal Scandium." R. THALÉN. 'Comptes Rendus,' July 5, 1880, vol. xci., p. 45; 'Chemical News,' July 30, 1880, vol. xlii., p. 60. (THALÉN only gives the wave-lengths of lines in the visible portion of the spectrum.)

"Spectral Researches on Scandium, Ytterbium, Erbium, and Thulium." TH. THALÉN. 'Journal de Physique'; 'Chemical News,' May 11, 1883, vol. xlvii., p. 217.

W. CROOKES. "On Radiant Matter Spectroscopy: Examination of the Residual Glow." 'Proc. Roy. Soc.,' February 1887, vol. xlii., p. 111. "Scandium, either in the form of earth or sulphate, phosphoresces of a very faint blue colour. Addition of lime does not bring out any lines."

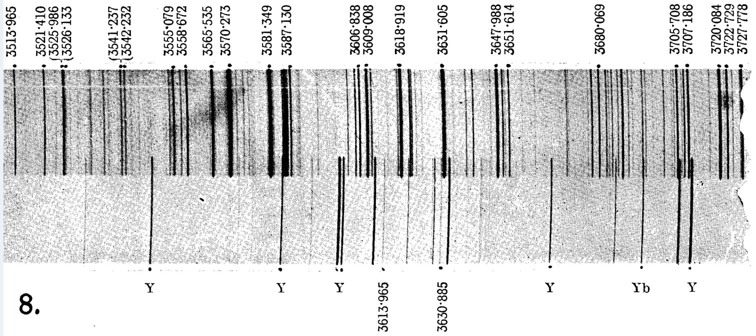
"The Arc Spectrum of Scandium, and its Relation to Celestial Spectra." By Sir NORMAN LOCKYER and F. E. BAXANDALL. 'Proc. Roy. Soc.,' February, 1905, vol. lxxiv., p. 538.

G. URBAIN ('Journal de Chimie-Physique,' February, 1906, vol. iv., p. 64) gives a passing reference to scandium as follows:—"In none of my fractions have I been able to observe the presence of scandium. I am led to think that this element does not belong to the group of rare earths, properly so-called. Sir W. CROOKES ('Chemical News,' vol. xci., p. 61) thinks he has detected this element in my gadolinia. [Quite true.—W. C.] The statement is denied by EBERHARD ('Zeit. Anorg. Chemie,' xlv., p. 374)."

THE SCANDIUM SPECTRUM.—SELECTED GROUPS OF CHARACTERISTIC LINES.

To economise space and avoid unnecessary complications, I give photographs of only those parts of the spectrum containing the most prominent scandium groups. The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to ROWLAND'S measurements. The lower halves contain the scandium lines, with their wave-lengths calculated from the iron standards.

There are also many strong lines in the ultra-violet spectrum of scandium between λ 3535·865 and λ 2300. I have not completed the measurements of these lines, and their description must form the subject of a subsequent communication.



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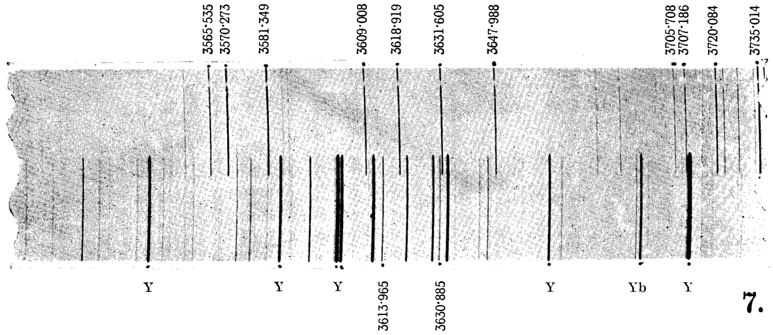
8. Spectrum of crude rare earths from keilhauite, also photographed in the same position as in Spectrum 5. It was from the rare earths from keilhauite that CLEVE prepared scandium.



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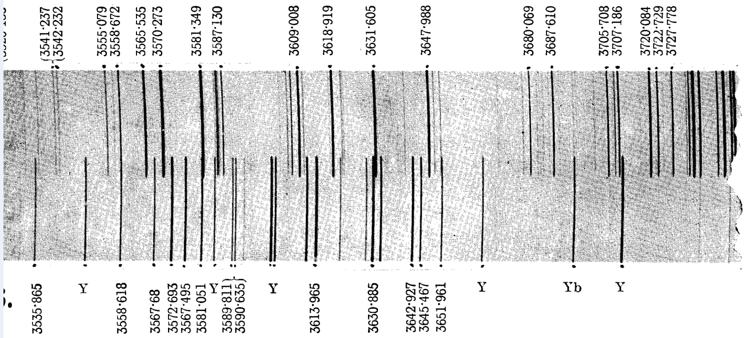

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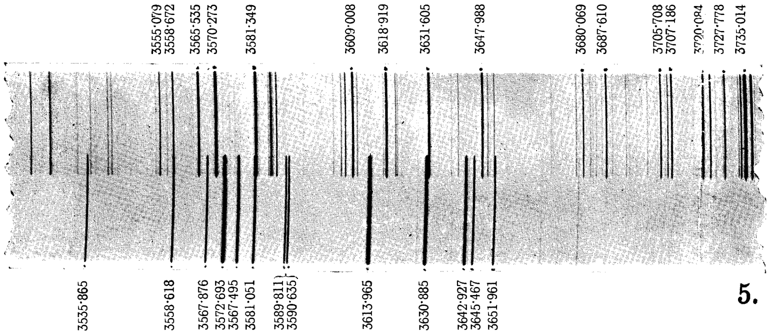

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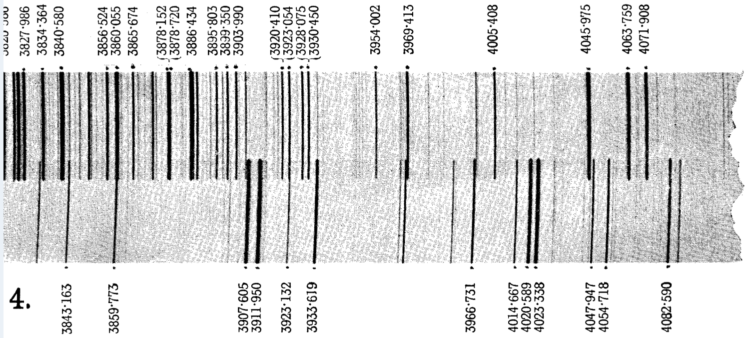

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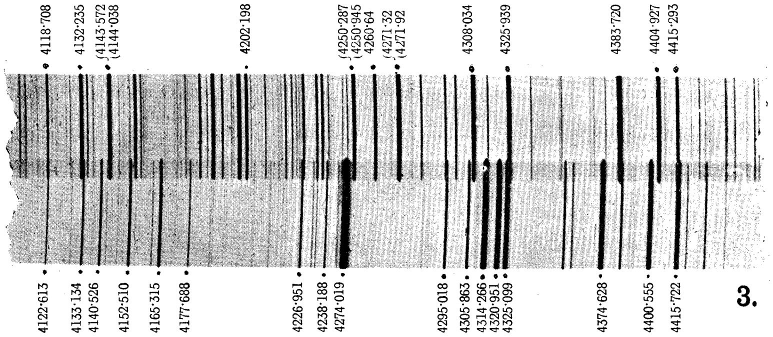

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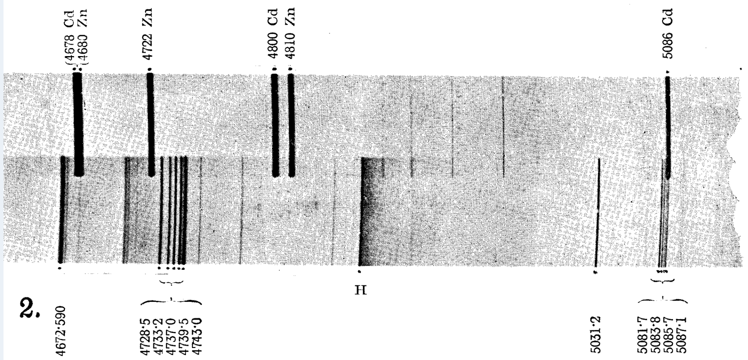

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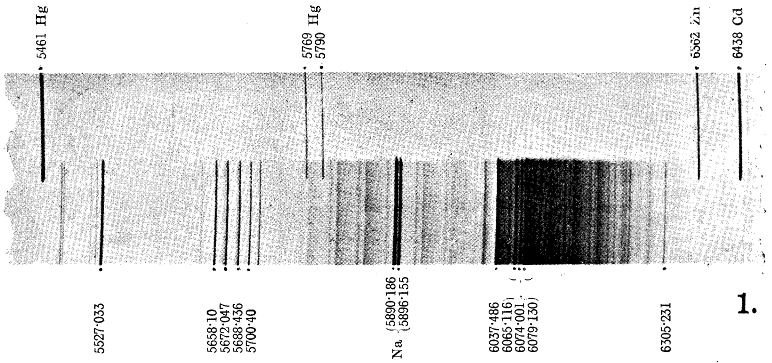

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1. Group of visible lines between λ 6305·231 and λ 5527·033.

In the part of the spectrum shown on strips 1 and 2 there are no iron lines suitable for standards. Here, therefore, I have used some good lines of zinc, cadmium, and mercury. Attention is drawn to the comparative intensities of the yttrium lines and the dominant line of scandium in the spectra from the wiikite, euxenite, and keilhauite earths. The spectrum of the earths from gadolinite is not given, as the dominant line of scandium in it is too faint to be reproduced.

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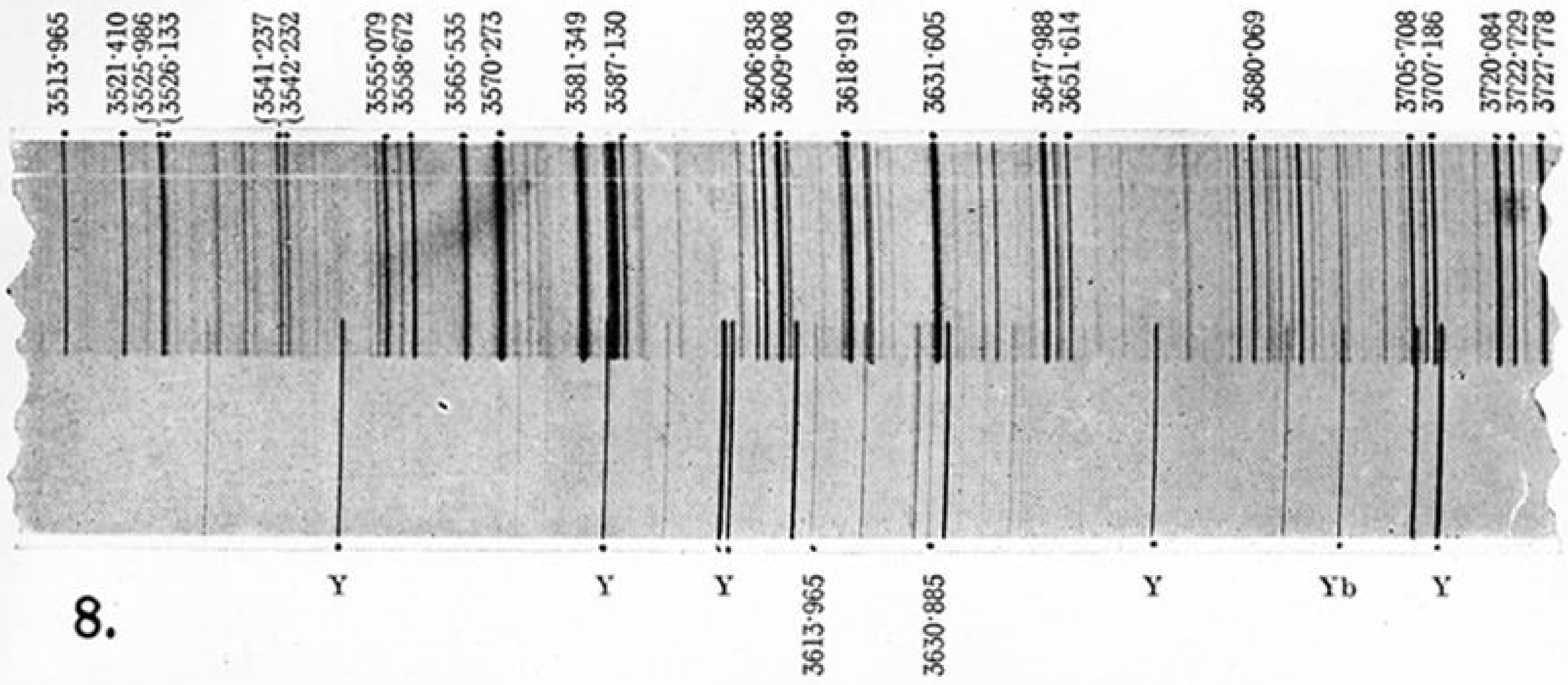

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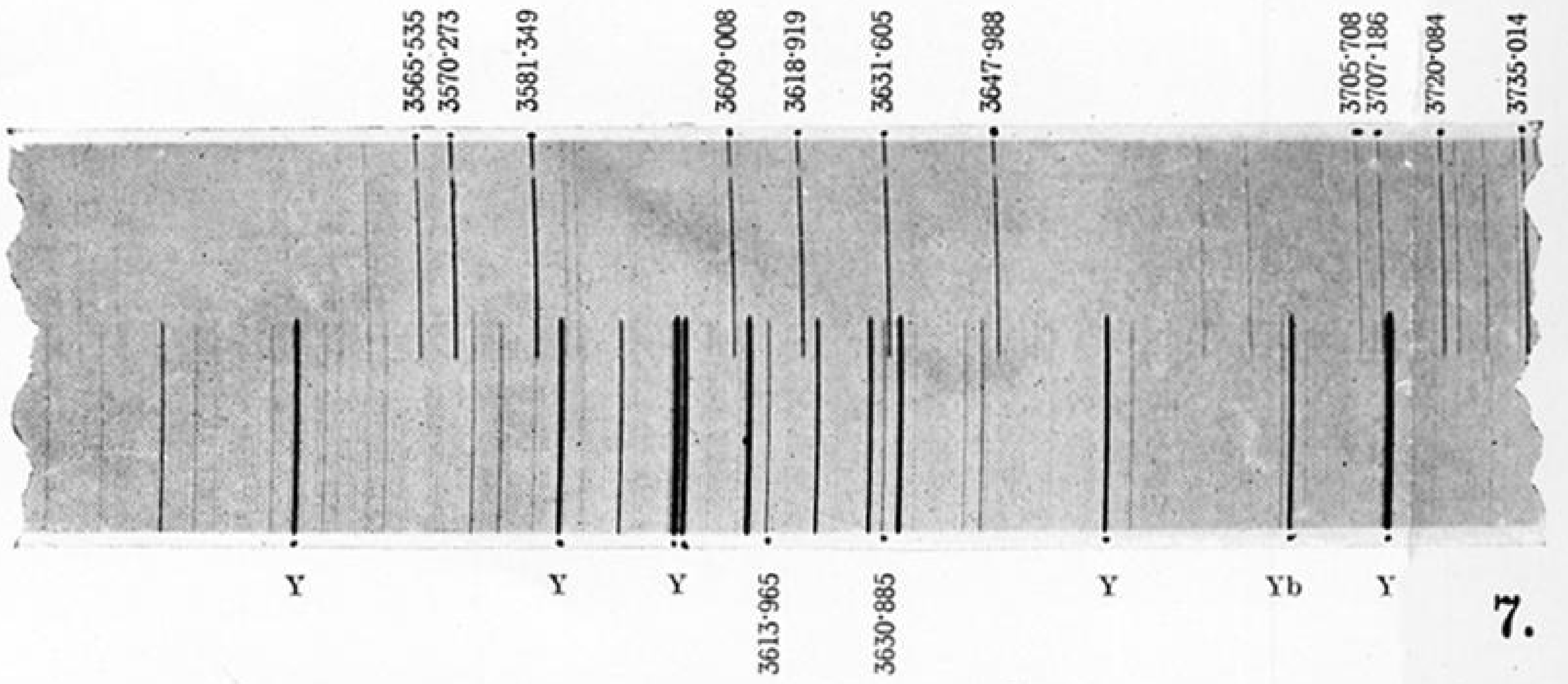

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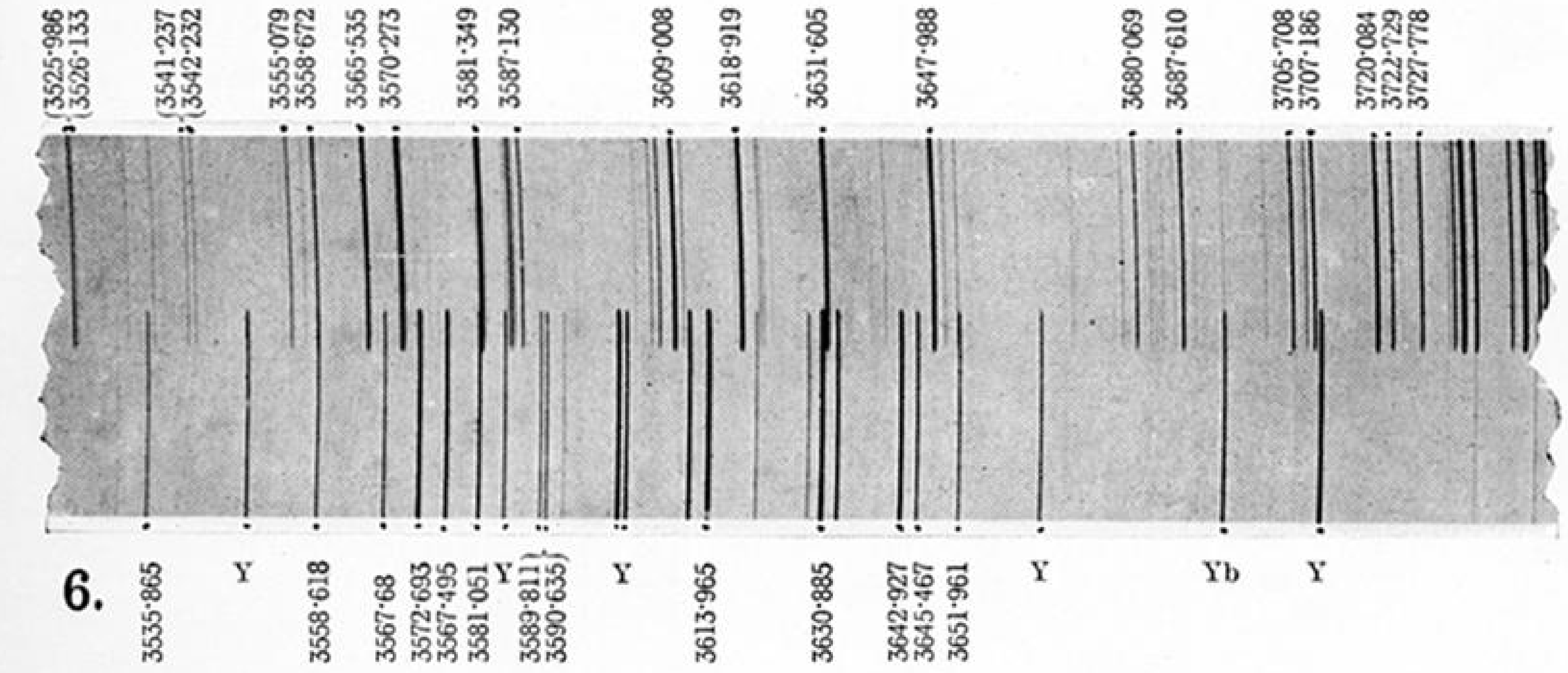

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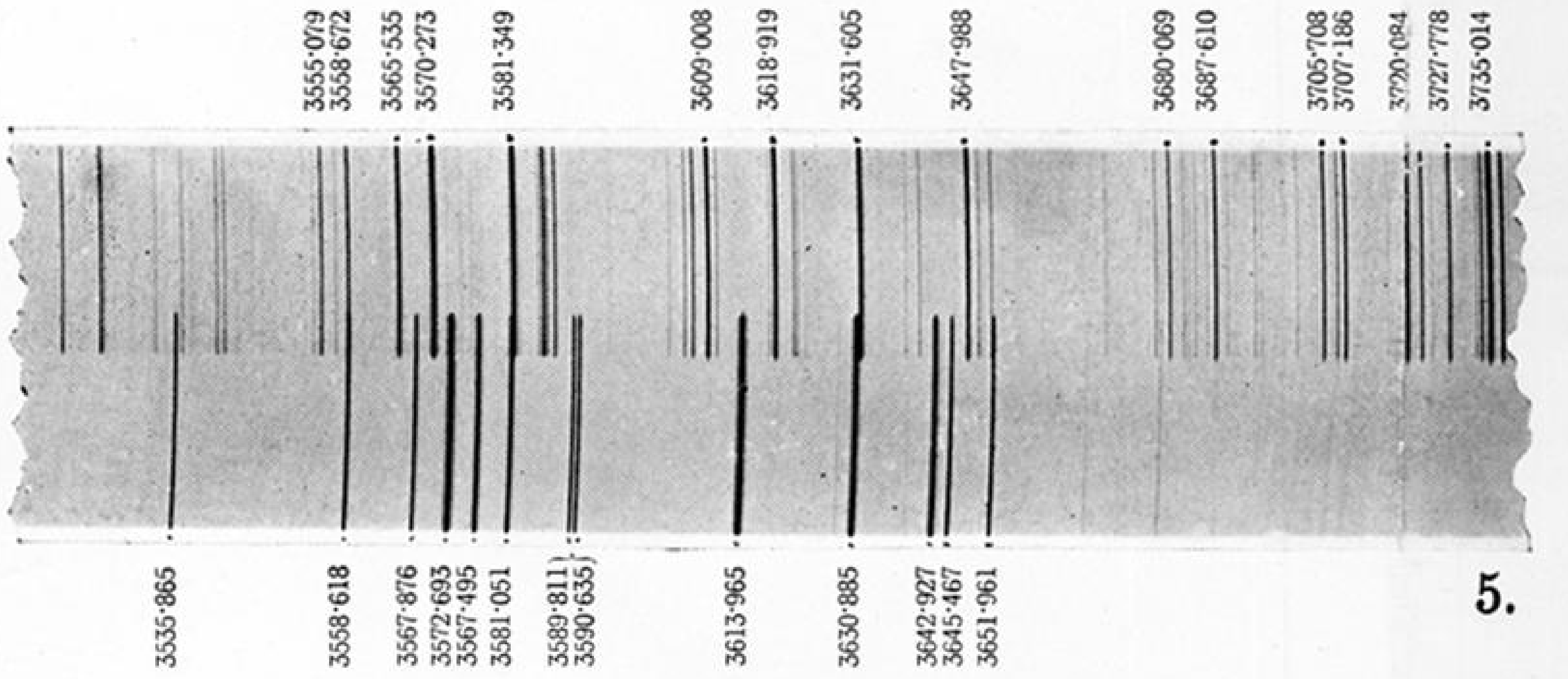

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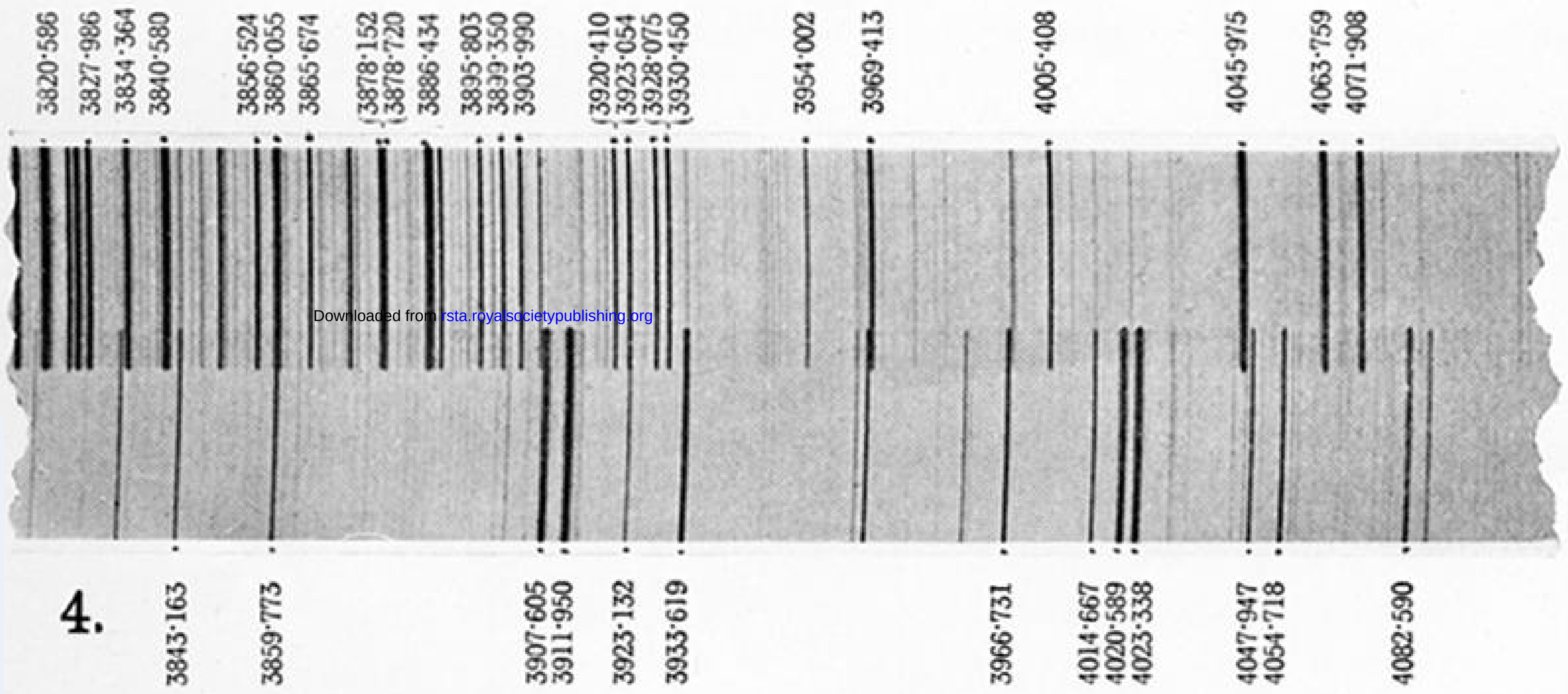

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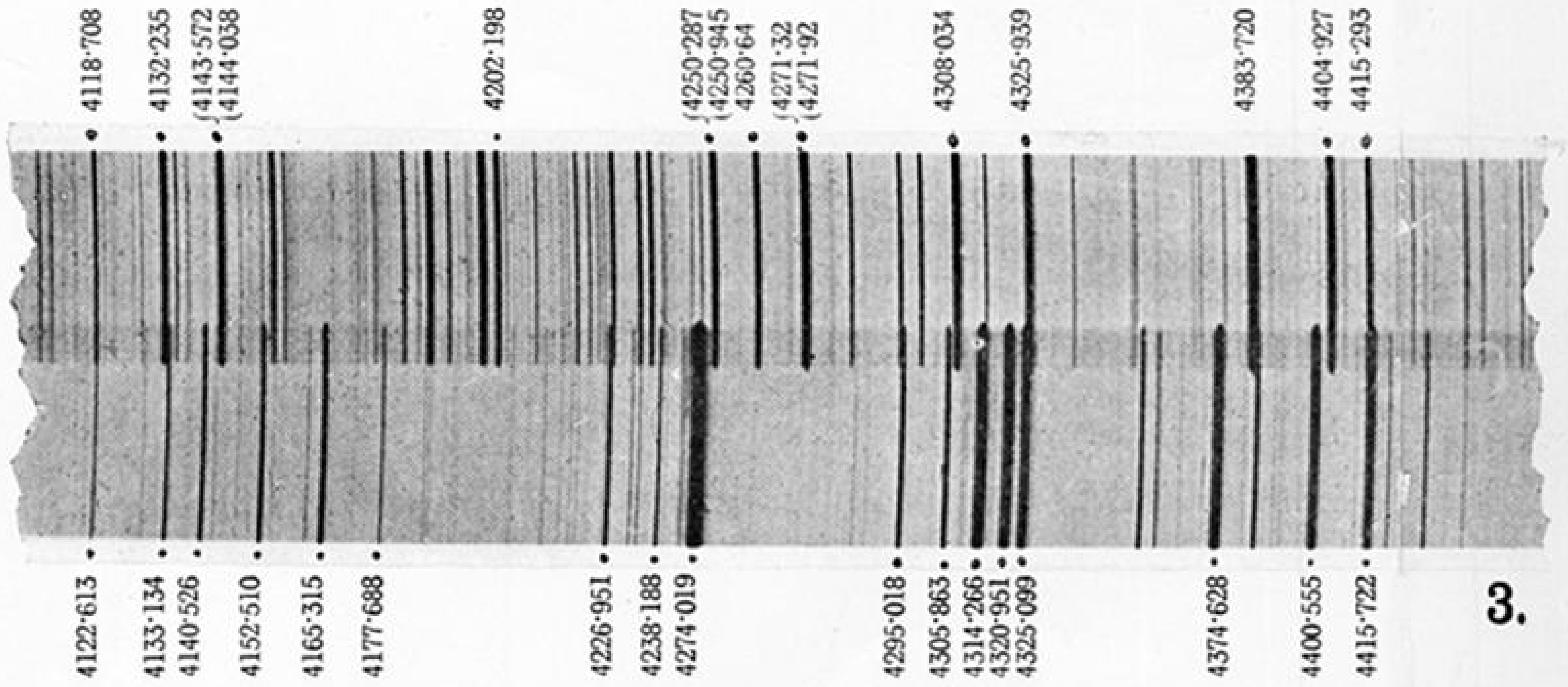

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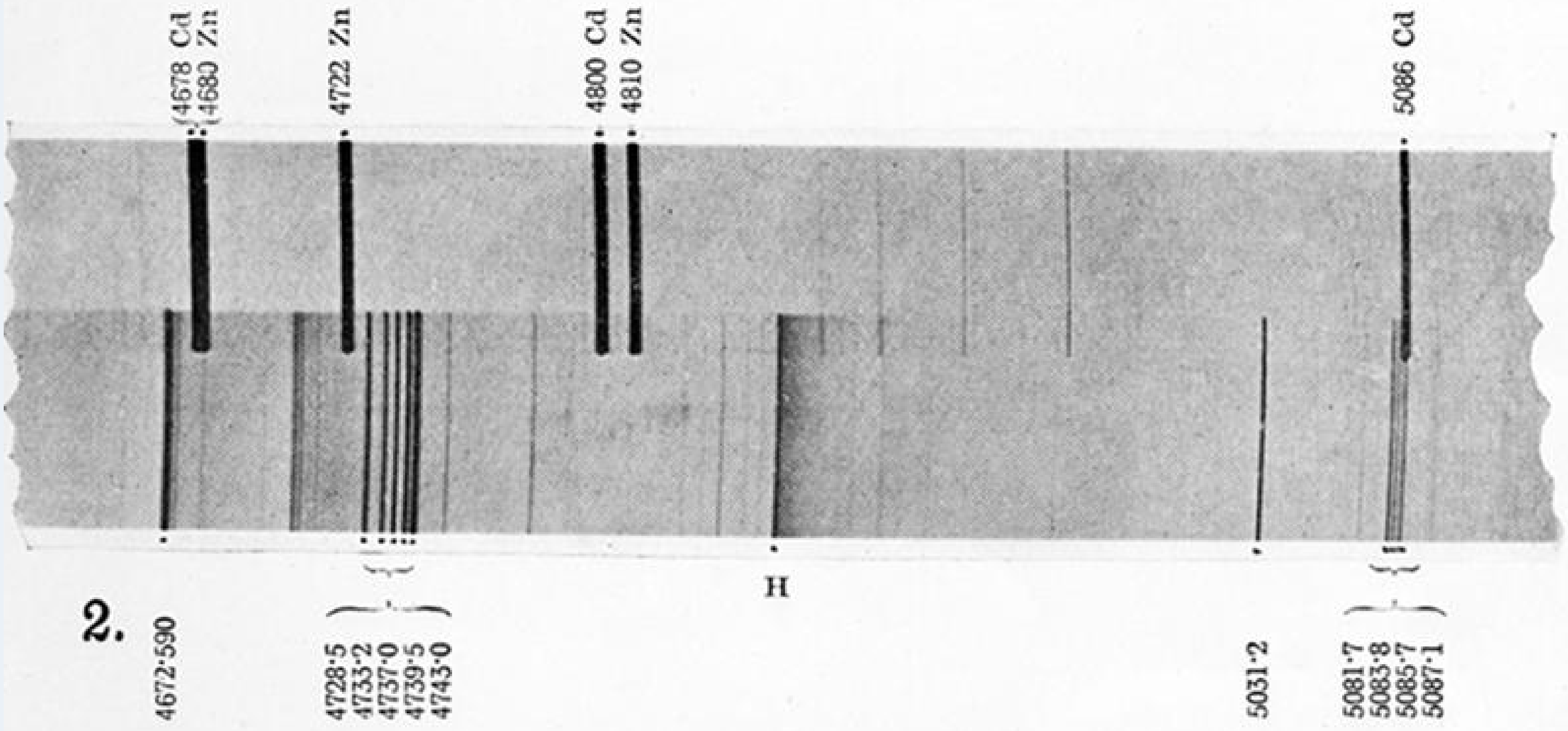

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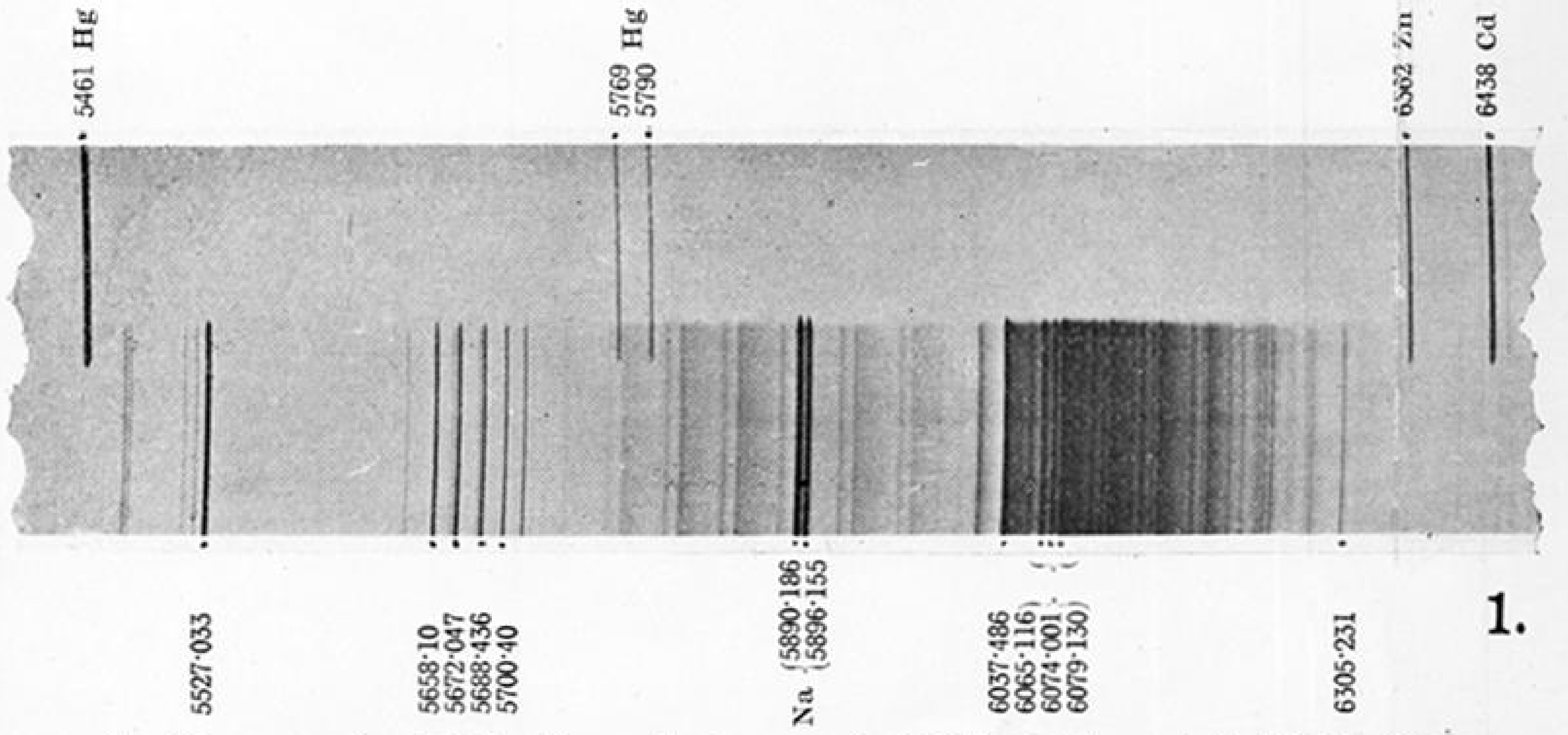

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