XIV. *On Radiant Matter Spectroscopy.*—Part II. *Samarium.*

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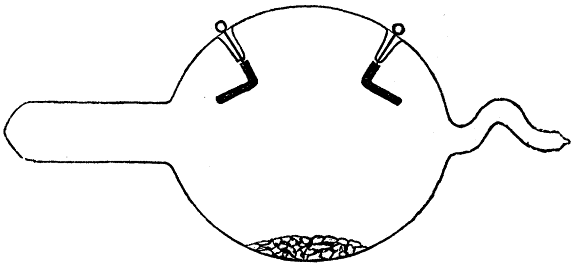
[Plate 75.]

Introduction.

90. In the concluding sentence of the Bakerian Lecture which I had the honour to deliver before the Royal Society, May 31, 1883, I said that the new method of Radiant Matter Spectroscopy there described had given me not only spectrum indications of the presence of yttrium as an almost invariable, though very minute, constituent of a large number of minerals, but had likewise revealed signs of another spectrum-yielding element. I stated that I had repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band. That this second spectrum was not then new to me is shown by a paper sent to the Royal Society in 1881,[*] in which I described a double orange band occurring in the phosphorescent spectrum of an earth less frequently met with than the "pale yellowish coloured earth" (since identified as yttria) which gave me the "red, orange, citron, and green bands."

Fig. 1.



91. The method adopted to bring out the orange band is to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness. It is then put into a radiant matter tube, of the form shown in fig. 1, and the induction spark is passed through it after the exhaustion has been pushed to the required degree. The anhydrous sulphate thus

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[*] Proc. Roy. Soc., vol. xxxii. (1881), p. 206.

left frequently shows the orange band in the radiant matter tube, though before this treatment the original substance shows nothing.

The Elimination of Mercury Vapour from Vacuum Tubes.

92. The presence of mercury vapour is liable to interfere with the spectrum indications, and when working in an entirely new field, where the mutual reaction of bodies one on the other is the subject of the research, it is always desirable to reduce the unavoidable constants to a minimum. In a tube exhausted in the ordinary manner by the SPRENGEL pump more mercury vapour is present than is generally supposed. Unless the tube is exhausted and sealed off without loss of time, mercury diffuses through the connecting tubes, and soon gets into the vessel under experiment. It is not easily detected by the spectroscope so long as the tube remains cold, but when the passage of the current has warmed the glass and the metal poles the mercury lines become distinctly visible, and the same result is obtained at once when the tube is heated by a lamp.[*]

The following experiment illustrates this behaviour of mercury:—A small radiant matter tube, having flat aluminium poles connected to platinum terminals passing

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[*] In incandescent lamps exhausted by means of a mercury pump, a peculiar blue phosphorescence is observed to fill the globe when the filament is raised much above its normal incandescence. This phenomenon has been examined and discussed by Mr. EDISON in America and by Mr. PREECE in England (Proc. Roy. Soc., vol. xxxviii., No. 236, p. 219). During the course of my work on the manufacture of incandescent lamps I have frequently noticed the same effect. Examined in the spectroscope the phosphorescent light filling the globe shows the mercury lines strongly. In order to examine this phenomenon more closely the following experiments were tried:—An incandescent lamp with fine carbon filament which had been plated up in vapour of carbon tetrachloride was placed in one of the sides of a Wheatstone bridge and connected with a dynamo-electric machine, where by means of a suitable rheostat it could be raised to any desired degree of incandescence. A spectroscope was adjusted so that the slit was opposite the rarefied space between the two limbs of the filament. With an E.M.F. of 64·5 volts, a current of 0·97 ampère, and a light of twenty candles, no lines were visible in the spectrum; on increasing the volts to 73·6 the current became 1·15 ampères, and the c. p. 43. At this stage flashes of blue phosphorescence filled the bulb at regular intervals of about ten seconds, and at the same instant the mercury lines were seen in the spectroscope, $\frac{1}{\lambda^2}$ 2984, 3006, 3354, and 5265 being most prominent. On increasing the E.M.F. to 81·3 volts, the current became 1·28 ampères, and the light seventy-four candles, the flashes of phosphorescent light became more frequent, pulsating very regularly once every three seconds, and at each flash showing the mercury spectrum strongly. The E.M.F. was next increased to 99·7 volts, and the ampères to 1·83; at this point the light was equal to 172 candles. The flashes of light became more and more frequent, rising quickly from once in two seconds till they occurred too rapidly to count, and the blue phosphorescence became continuous and seemed to fill the globe. The mercury spectrum at this stage was permanent, and most of its lines could be detected. The flashes of light were probably owing to some such action as this:—the hot filament offering a considerable resistance to the passage of the current, the long length of insulated wire in the circuit (about half a mile, including the lamps used for house-lighting) charged up like a condenser and then at intervals discharged through the highly rarefied vapour in the bulb.

through the glass, was sealed to the pump and quickly exhausted. An induction current was immediately passed through, and the light examined in the spectroscope. No mercury lines were detected. The tube was then heated strongly, the spectroscopic examination being continued: no mercury lines were seen. The apparatus was then allowed to rest for a day, and the experiments were repeated. In the cold no mercury lines could be seen, but on heating the tube they became distinctly visible.

93. The tube was then exhausted to the highest possible point, and sealed off. In the cold it was impossible to get an induction-spark through the tube—it was absolutely non-conducting. However, on heating the tube with a BUNSEN flame, keeping the coil going all the time, suddenly the current passed, lighting up the inside of the tube with a greenish-blue light, in which the spectroscope showed strong mercury lines. On allowing the tube to cool it again became non-conducting, and the experiment could be repeated.

This shows that in a vacuum-tube which is so highly exhausted as to be non-conducting there is plenty of mercury present to carry an induction current, only it is not in the form of vapour, but is condensed on the metallic poles or on the sides of the glass.

94. It is much more difficult than is generally supposed to keep mercury vapour from diffusing itself into the experimental tubes. Gold-leaf was packed loosely in a tube about 2 feet long, which was then interposed between the pump and the radiant matter tube. This answered for a short time, but whilst it certainly kept back some of the mercury, it let much through.

For a long time I used a tube about 2 feet long, packed with coarsely powdered sulphur. This is effectual at first, but there is a liability of sulphur vapour getting into the tube, and this might be as disastrous as mercury. The sulphur was therefore kept out by interposing another tube containing finely divided copper. This, however, was not quite effectual: after a time mercury was found to have run the gauntlet of both sulphur and copper. It is of no use trusting to a solid reagent to absorb a gaseous body. Where the gas and solid meet there may be action, but some of the gaseous molecules are sure to get through without coming within the solid's sphere of attraction.

95. I finally adopted the following plan, which answers perfectly so far as my experiments have yet gone:—Sulphur is first prepared by keeping it fused at a high temperature till bubbles cease to come off, so as to get rid of water and hydrogen compounds. It is then allowed to cool, and is then pounded and sifted so as to get it in the form of granules averaging a millimètre in diameter. A glass tube, a centimètre in diameter and about 2 feet long, is lightly packed for half its length with this sulphur, and next about 2 inches of iodide of sulphur (I_2S_2) is added, and the rest of the tube is then filled up with sulphur. Ignited asbestos is packed in at each end to keep the sulphur from blowing out whilst the vacuum is being made, or from being sucked through when air is suddenly let in. This contrivance entirely

keeps mercury vapour from passing through, since the iodide of sulphur holds its iodine very loosely, and fixes the mercury in the form of non-volatile red iodide. A glass tube containing finely divided copper must follow in order to keep sulphur out. With this blockade interposed between the pump and experimental tubes I have been unable to detect mercury vapour in any of the tubes, whether in the cold or on heating them.

Mixed "Citron" and "Orange" Spectra.

96. Since the date of my last paper I have devoted myself to the task of solving the problem presented by the double orange band first observed in 1881. With the yttrium experience as a guide it might be thought this would not be a difficult task, but in truth it helped me little beyond increasing my confidence that the new like the old spectrum was characteristic of an element. The extreme sensitiveness of the test is a drawback rather than a help. To the inexperienced eye one part of "orange band" substance in ten thousand gives as good an indication as one part in ten, and by far the greater part of the chemical work undertaken in the hunt for the spectrum-forming element has been performed upon material which later knowledge shows does not contain sufficient to respond to any known chemical test. It is as if the element sodium were to occur in ponderable quantity only in a few rare minerals seldom seen out of the collector's cabinet. With only the yellow line to guide, and seeing the brilliancy with which an imponderable trace of sodium in a mineral declares its presence in the spectrum, I venture to think that a chemist would have about as stiff a hunt before he caught his yellow line as I had to bring my orange and citron bands to earth.*

Chemistry, except in few instances, as water-analysis and the detection of poisons, where necessity has stimulated minute research, takes little account of "traces;" and when an analysis adds up to 99·99, the odd 0·01 per cent. is conveniently put down to "impurities," "loss," or "errors of analysis." When, however, the 99·99 per cent. constitutes the impurity and this exiguous 0·01 is the precious material to be extracted, and when, moreover, its chemistry is absolutely unknown, the difficulties of the problem become enormously enhanced. Insolubility as ordinarily understood is a fiction, and separation by precipitants is nearly impossible. A new chemistry has to be slowly built up, taking for data uncertain and deceptive indications, marred by the interfering power of mass in withdrawing soluble salts from a solution, and the solubility of nearly all precipitates in water or in ammoniacal salts when present in traces only. What is here meant by "traces" will be better understood if I give an instance. After six months' work I obtained the earth didymia in a state which most chemists would call absolutely pure, for it contained not more than one part of

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*So recently as the year 1880 a high authority on blowpipe chemistry seriously argued that the yellow coloured flame "which is ascribed to sodium" is not caused by that metal, but is due to "chemical water." ('Chemical News,' vol. xli., p. 159, April 2, 1880.)

impurity in five hundred thousand parts of didymia (131). But this one part in half a million profoundly altered the character of didymia from a radiant-matter-spectroscopic point of view, and the persistence of this very minute quantity of interfering impurity entailed another six months' extra labour to eliminate these final "traces" and to ascertain the real reaction of didymia pure and simple (131).

For a long time the "citron-band" and the "orange-band" spectra were confounded. That they were due to two different states or kinds of matter was not easily decided, since in all the early experiments I was dealing with a mixture; consequently the spectra obtained were not only mixed but differed considerably in the relative intensities and faintness of the different lines (146).

97. At last having separated yttria and obtained its spectrum pure (71), the characteristic lines in the other spectrum or spectra could be provisionally mapped out by difference, and a systematic hunt was instituted for the new "orange band" substance, which to avoid periphrasis was termed x. Naturally my thoughts turned to samarskite and the yttria earths. A wide, prolonged survey over every available substance had convinced me that the number of bodies giving a discontinuous phosphorescent spectrum is extremely limited, and to be counted on the fingers of one hand; and having satisfactorily mated one of these spectra to yttria it became in the highest degree probable that the twin spectrum should belong to one of the nearest chemical associates of yttria.

Chemistry of the "Orange-Band" forming Body.

98. At first it was necessary to take stock, as it were, of all the facts regarding x which had turned up during the search for the orange band. In the first place x is almost as widely distributed as yttria, generally occurring with the latter earth. Sometimes, however, the orange band was strong where the citron band was almost or quite absent. It is almost certainly one of the earthy metals, as it occurs in the insoluble oxalates, in the insoluble double sulphates, and in the precipitate with ammonia. It is not precipitated by sodic thiosulphate, and, moreover, it must be present in very minute quantities, since the ammonia precipitate is always extremely small, and as a rule x is not found in the filtrate from this precipitate.

99. At this stage of the enquiry the chemical reaction of x were much more puzzling than with yttria. At the outset an anomaly presented itself. The orange band was prone to vanish in a puzzling manner. Frequently an accumulation of precipitates tolerably rich in x was worked up for purposes of concentration, when the spectrum reaction suddenly disappeared, showing itself neither in precipitate nor filtrate (3, 101, 108, 115); whilst on other occasions, when following apparently the same procedure, the orange band became intensified and concentrated with no apparent loss. The behaviour of the sulphate to water was also very contradictory; on some occasions it appeared to be almost insoluble, whilst occasionally it dissolved in water readily (115).

100. For some time I debated whether the orange-band spectrum might not be a

mere modification of the yttrium spectrum induced by the presence of some extraneous body. We know that yttria *per se* has little or no phosphorescence (75), that this power chiefly resides in the ignited sulphate. Might it not happen that some other earth with molecules peculiarly sensitive to the longer vibrations would confer upon yttria some of its sensitiveness to the red end of the spectrum?

It would be too much like a repetition of my paper on the yttrium spectrum quest were I to detail the numerous experiments and false starts with samarskite, orangite, thorite, strontianite, cœlestine, perofskite, cerite, coral, &c.; but I may be permitted to extract from an enormous mass of chronicles which must remain unpublished, some few experiments which will usefully emphasize what I may call the nodal points in this research.

"X" from Samarskite.

101. It was to be expected that samarskite would contain *x*. It occurred, however, very little in the yttria group, but was found with the decipia residues (47, 49), or the earths forming, with potassium, insoluble double sulphates,—ceria, lanthana, didymia, decipia, samaria, together with a little thoria and zirconia. These residues were dissolved in hydrochloric acid, precipitated with ammonia, washed till free from potassic salts, re-dissolved, and precipitated as oxalates. The filtrate was set aside in Winchester quart bottles, and after standing for some weeks a further quantity of insoluble oxalates was found deposited at the bottom of the bottles. These were collected, and appeared to be very rich in *x*; but on attempting to work them up vexatious anomalies constantly started up: suddenly the orange band would disappear, and after being lost sight of for a week or two, would return in a manner equally unaccountable (3, 99, 108, 115).

Thorite and Orangite.

102. Early in my research thorite and orangite (26) had given a brilliant spectrum, afterwards identified with that of yttria (70). When hunting for *x* some of the insoluble double sulphates from these minerals (32) were treated like the samarskite double sulphates to remove potassium (101), and examined in the radiant matter tube. Here, also, was found the orange-band spectrum, quite different from the yttrium spectrum of the soluble sulphates; but, as usual, it behaved in a most capricious manner.

Perofskite.

103. An American friend, Mr. GEORGE F. KUNZ, with great kindness sent me some pounds' weight of the rare mineral perofskite (calcic titanate), in fine crystals, from Magnet Cove, Arkansas, together with a large number of specimens of associated minerals from the same locality. The perofskite was found to be richer in *x* than any mineral yet examined. At great sacrifice of material a small portion of an earthy

body was obtained giving the orange-band spectrum more brilliantly than I ever had seen it before. Analysis failed to detect anything in it but lime (5,9), the flame spectrum showed lime, and the atomic weight came out $RO = 55{\cdot}3$, CaO being 56.

Calcite.

104. Mr. LETTSOM, understanding I was engaged in quest of an unknown body supposed to be associated with calcium, most kindly sent me specimens of rare and curious minerals; and through his good offices Professor ALBIN WEISBACH presented me with an extensive set of calcites; these, prior to the invention of the spectroscope, had been measured by Professor A. BREITHAUPT, who, owing to the discordant measurements, held what is known as "calcium" to consist of two or more allied elements, which as yet chemists were unable to separate.

These calcites were treated as usual and examined most carefully in the radiant matter tube. In one of them only was a trace of yttria found, but the orange-band spectrum was very faintly seen in six of the thirteen specimens. The others shone with the usual greenish-blue phosphorescence of calcic sulphate, giving no lines or bands in the spectrum.

I am also indebted to Mr. LETTSOM for a specimen of calcite from Branchville, S. Carolina, which, when heated, has the curious property of glowing strongly with a golden-yellow light showing a faint continuous spectrum. In the radiant matter tube the phosphorescence was very brilliant, but there was no discontinuity in the spectrum, only a concentration of light in the red portion.

Dolomite.

105. Another curious mineral, for which I am also indebted to Mr. LETTSOM, is a granular dolomite from Utah. When scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it Hell-fire Rock. By itself in the radiant matter tube it brightly phosphoresces with a reddish light, showing no bands, but a concentration of light in the red. Treated with sulphuric acid in the usual manner, and then examined in a vacuum tube, a similar continuous spectrum was observed. Chemical analysis showed that it was a nearly pure double calcic and magnesic carbonate, with a little iron, alumina, and phosphoric acid.

Amongst other minerals found to give the orange band spectrum I may mention zircon, euxenite, tyrite, fergusonite, rhabdophane, cerussite, apatite, galliferous blende, argentiferous galena, anglesite, harmotome, allanite, cerite, magnesite, oolite from Bath, &c.

Coral.

106. In my former paper (88) I mentioned that a specimen of pink coral contained about a half per cent. of yttria, judging from the very strong yttrium spectrum it

gave in the vacuum tube. Professor MARTIN DUNCAN has identified this specimen as a *Gorgonia* of the genus *Melithœa.* Another recent coral, *Mussa sinuosa,* gave equally strong indications of yttrium. By the kindness of Professor DUNCAN I have since been enabled to submit a large number of corals to spectrum examination in the radiant matter tube. Nearly all showed more or less discontinuity in their phosphorescent spectra, but as in the yttrium spectrum research I obtained only two specimens giving a brilliant yttrium spectrum, so in the present quest I have found only two corals giving a strong orange-band spectrum. One is a *Pocillopora damicornis,* from Singapore and most of the Pacific Islands which have reefs, one of the old group of tabulate corals. A fragment of this coral, treated with sulphuric acid and examined in the radiant matter tube, gave as brilliant an orange-band spectrum as I had ever seen. The other is of the species *Symphyllia,* close to *Mussa,* a reef-builder from the same locality as the *Mussa* which gave so much yttria.

Sea-water.

107. These results induced me next to try sea-water. Ammonic oxalate and hydrate gave a white precipitate, which was filtered off and washed. The oxalate was then ignited, dissolved in nitric acid, and the solution supersaturated with ammonia and boiled. The resulting precipitate, tested in the radiant matter tube, showed the orange-band spectrum very well.

"X" in Strontium Minerals.

108. The orange-band spectrum in the radiant matter tube at first sight bore a close resemblance in the red region to the flame spectrum of strontium; the two spectra therefore were examined together, and on comparing them a near coincidence was observed between two lines in the orange. Was it possible that the sought-for element was strontium?

This led to an examination of the strontic nitrate used in the flame reaction. When converted into sulphate and tested in the radiant matter tube the experiment succeeded only too well. The orange-band spectrum came out brilliantly.

Other commercial strontium compounds were now tested. Yttria was found almost universally, but the orange band was capricious; the nitrate generally showed it well, caustic strontia sometimes, chloride as a rule not at all. These were from different makers. The source was enquired for, and in a few weeks my laboratory was filled with large specimens of Gloucestershire, Italian, and Sicilian cœlestine, and Scotch, Italian, and German strontianite, together with waste-products, mother-liquors, and every commercial salt of strontium. The kindness of the manufacturers was great, and I regret that the outcome was not more notable.

Italian cœlestine showed a good orange-band spectrum when crushed and examined in the tube without any chemical treatment. After getting the mineral into solution by fusion with sodic carbonate, &c., the x could be concentrated by fractionally precipitating with alkaline carbonates (coming down in the first fractions). The sulphate produced from this precipitate also showed the desired spectrum.

This sulphate was digested for some time in warm ammonic carbonate, and now the old distressing anomalies re-commenced. On most occasions, when working roughly on a scale of a few grammes, all the x was found in the filtrate on evaporation and ignition. When, however, I took identically the same material, and worked it up more carefully, in pounds or hundredweights, it sometimes gave nothing at all, sometimes only a *ridiculus mus* on the smallest sized filter, got from a mountain of raw material. This was at first accounted for by the want of homogeneity of the mineral. The real explanation, however, was not discovered till long after (115).

A quantitative estimation was attempted of the amount of x substance got from Italian cœlestine. 630 grms. gave 1·525 grm., or 0·24 per cent. Analysis showed this to be chiefly strontic sulphate, and the atomic weight of the metal was close to that of strontium.

Is "x" a Mixture?

109. For a considerable time strontium minerals and salts only were worked upon, these being considered the cheapest and most fruitful sources of x. A considerable quantity of material was thus accumulated, showing the desired spectrum with great brilliancy. When, however, attempts were made to separate the spectrum-forming body from the accompanying elements, as strontium, calcium, &c., all the foregoing anomalies were displayed. Ultimately two portions of substance were produced—a precipitate (113) containing the supposed new element, and a filtrate, containing the strontium, calcium, and other impurities. Neither the precipitate nor filtrate tested in the usual manner showed the orange band anything like so well as the material before such separation, and indeed at this stage of the experiments it frequently vanished altogether.

Some of the filtrate and precipitate were now mixed together, treated with sulphuric acid, and tested as before: they gave the orange-band spectrum as brightly as did the original substance. The ammonia precipitate was too small for analysis, but judging from its origin it might contain any or all of the rare earths. Chemical analysis showed nothing but a calcium salt in the filtrate.

110. Could it be that the union of two bodies was necessary to give this spectrum, and that calcium was one of these? Could the other constituent be of the nature of an acid such as boric, or a halogen like fluorine?

Many experiments were tried to test this hypothesis. Pure Iceland spar was dissolved in acid, a little of the above described precipitate added, and the mixture tested in the usual way. The orange band appeared again.

Every conceivable mixture was now made of lime with other bodies, but whilst I frequently obtained faint indications of orange band there was never sufficient to satisfy me that I had artificially formed the spectrum-bearing body; the traces observed were evidently due to the all pervading presence of the sought for body.

So far all had been contradictory and disheartening. Analogy with the yttrium results failed to throw light to guide through the gloom. The hypothesis that the body sought was an earth, widely diffused in minute quantities only, and that its anhydrous sulphate gave a phosphorescent spectrum in the radiant matter tube, had guided me a certain distance and then led me widely astray. A new factor must now be taken into account—the presence of a calcium compound appeared to be necessary. An earthy body which, when treated and tested in the usual manner, fails to show the faintest glow of an orange-band spectrum, can by admixture with calcic sulphate be made to yield a pure and brilliant spectrum, rivalling in clearness and beauty that given by yttric sulphate.

111. Of the two components of the phosphorescing body—calcium and x—which is the necessary and which is the variable factor?

This question did not appear difficult to answer. In the first case the calcium must be kept the constant, and x be made the variable quantity.

A piece of pure colourless Iceland spar—the sulphate from which had been proved to phosphoresce normally with a greenish-blue light, without bands or concentration in any part of the spectrum (164)—was dissolved in hydrochloric acid, and mixed with about 10 per cent. of various metallic sulphates. Sulphuric acid was added, the mixture evaporated to dryness, ignited, and tested in a radiant matter tube. The bodies thus used to replace x, in addition to the more common earths, were the earths from samarskite—enumerated in the first part of this paper (40)—in as pure a state as I could get them, together with various earthy precipitates, oxalates, &c., obtained from different minerals during the preceding operations.

These experiments resulted in an *embarras de richesse.* Whereas, hitherto, I had considered the orange-band-forming body rare and sparsely distributed I now found it sharing with yttrium the attribute of ubiquity. The answer to my question was too full, and left me again in doubt as to whether calcium or x was the variable quantity.

The yttrium spectrum turned up in this series of experiments about as frequently as the orange-band spectrum. I knew that in such cases yttrium was present as an impurity; might it not be that the almost universal occurrence of the orange-band spectrum was equally caused by a minute but varying quantity of x in the earths under test?

112. I took them one by one and submitted them to further severe chemical treatment, fractionally precipitating them, in cold dilute solution, with weak ammonia, or fractionally crystallising their oxalates from nitric acid. As the purification progressed the orange-band spectrum generally lessened in intensity till in the case of many earths it faded out altogether, and in most of them it gave evident indications of

being extraneous to the earth itself. In some instances, however, the spectrum increased in intensity; moreover, when the purified earth showed any diminution of the orange band the eliminated impurity always showed the orange band in an exalted degree. I drew from these experiments the inference that x was a definite element, as widely distributed, or nearly so, as yttrium, but requiring admixture with a calcium compound to bring out its phosphorescent properties.

113. Next I had to ascertain if the calcium could be replaced by any analogous body. In this case, therefore, the x was kept constant whilst the calcium was replaced. An ammonia precipitate (109) from a rich accumulation of orange band substance was chosen as the x. Tested in the usual manner, by itself, it showed nothing, but mixed with lime it gave the orange-band spectrum very bright and pure.

The metals used to mix with it were in the form of sulphates—strontium, barium, glucinum, zirconium, thorium, magnesium, zinc, cadmium, lead, copper, silver, cerium, lanthanum, didymium, aluminium, manganese, tin, bismuth, antimony; also silicic, titanic, tantalic, tungstic, molybdic, and niobic acids. More than half of these bodies possessed the property of conferring "orange-band" phosphorescence on the precipitate under examination, although by themselves they evinced no power of giving a phosphorescent spectrum.

Explanation of foregoing Anomalies.

114. In this manner the remarkable fact was established, that the x I sought was an earth which of itself could give little or no phosphorescent spectrum in the radiant matter tube, but became immediately endowed with this property by admixture with some other substance, which substance likewise by itself had no power of phosphorescing with a discontinuous spectrum.

Of the great number of bodies used to mix with the earth x in these experiments, which acted best? It was not easy to try comparative experiments at this early stage; ultimately I came to the conclusion that lime, if not the best, was as good as any.

115. These results afford a full explanation of the anomalies which had so long hampered my endeavours to repeat on a large scale experiments which, when working with small quantities, had given good results (99, 101, 108). The preliminary experiments were intended to ascertain whether the desired orange band was present or not. Natural impatience led to hurried operations and defective washing of precipitates, and thus some of the necessary *lime* was left with the phosphorescing body. The subsequent larger operations were performed in a more systematic manner with the object of securing as large a yield of substance as possible. The precipitates were thoroughly washed, the lime was more completely thrown out, and the sought-for earth, although obtained, refused to reveal itself by the spectroscope and radiant matter tube.

The contradictory behaviour of the sulphate to water (99) was now easily explained. The insoluble crystals, which from the brilliancy of their phosphorescent spectrum I had at first mistaken for the nearly pure sulphate of *x*, were merely calcic or strontic sulphate contaminated with perhaps not more than the one ten-thousandth part of *x* sulphate which it had carried down with them on crystallising.

"*X*" *in Cerite.*

116. In the corresponding yttrium research I was aided materially by the fact that the sought-for earth did not give an absorption spectrum (42). This enabled me to throw out a large number of obscurely known elements, and I therefore early endeavoured to ascertain whether the supposed new earth, *x*, did or did not give an absorption spectrum. At first I could not decide one way or the other. I frequently obtained a good orange-band spectrum when the solutions gave no trace of absorption spectrum, whilst on other occasions the solution showed good didymium and other bands. Gradually, however, it was noticed that whenever the didymium absorption bands were strong the orange-band spectrum was also particularly brilliant. Moreover, amongst the earths enumerated in par. 113 as mixed with lime in the quest for *x*, I have mentioned that some of them gave the orange-band spectrum with increased intensity; the earths of the cerium group were the most noteworthy, and these considerations made it probable that here would be found the location of *x*.

117. On a former occasion, when searching for the citron-band-yielding earth, and examining cerite (22 to 25), I made use of the potassic-sulphate method of separating the two great sub-groups, viz., the cerium and the yttrium earths; the former giving insoluble, and the latter soluble, double sulphates. I said (23):—

"The precipitated double sulphates were dissolved in hydrochloric acid, and the earths precipitated as oxalates. After ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and didymia were tested in the radiant matter tube, but the merest trace only of citron band was visible."

A repetition of the above experiment produced similar results. The contents of the tube were now removed, mixed with lime and excess of sulphuric acid, ignited, and again tested in the tube. This time the orange-band spectrum came out very brilliantly, showing in a striking manner the necessity of supplementing *x* with some other earth to bring out its phosphorescing properties.

The cerium group, to which *x* was now almost certainly traced, consists of cerium, lanthanum, didymium, samarium, and perhaps yttrium-α (136). The other metals, enumerated in par. 101 as being precipitated by potassic sulphate, were found not to phosphoresce with a discontinuous spectrum, either alone or when mixed with lime.

Analysis of Cerite.

118. The first necessity was to get the earths ceria, lanthana, and the mixture hitherto called didymia, in a pure state, for my so-called pure earths of this group all showed the orange band in more or less degree.

About 14 lbs. of cerite were finely ground, made into a thick paste with strong sulphuric acid, and heated to drive off excess of acid. The mass became of a white or pale grey colour. This was digested in cold water, filtered, and the residue well washed with cold water.

To the filtrate oxalic acid was added, which precipitated all the earths, with any lime, &c., that might be present, as oxalates. It saves time at first only to aim at a partial separation of the mixed earths, and for this purpose it is well to proceed as follows :—The dried oxalates are boiled with strong nitric acid till completely decomposed, the nitrates are evaporated to dryness, mixed with three times their weight of nitre, and fused at the lowest temperature at which nitrous fumes come off; the residue is digested in water, filtered, and washed. The insoluble residue, of a pale yellow colour, consists of ceric oxide and basic ceric nitrate, with a little of the other oxides, whilst the filtrate contains the bulk of the lanthanum, didymium, and samarium.

Separation of Ceria, Lanthana, Didymia, and Samaria.

119. To free the lanthanic, didymic, and samaric nitrates from the last traces of cerium it is necessary to fuse them again very gently with three or four times their weight of potassic nitrate, at a temperature just sufficient to cause slight decomposition. The operation of fusing must be repeated on the evaporated filtrate many times to throw out all the cerium.

The ceric oxide, or basic nitrate obtained, is freed from any didymium by retreatment with nitric acid and fusion as above; the presence of didymium being indicated by its brown colour or by the absorption spectrum of the solution.

120. The separation from each other of lanthana, didymia, and samaria is a most laborious process, and the amounts of these earths, obtainable in anything like a pure state, is small, compared with the mass of material worked up. The solution of the nitrates of these elements is made perfectly neutral, diluted to such a strength as to contain about 1 per cent. of the oxides, and a very dilute solution of ammonia is added, about 0·1 gramme NH_3 in 500 cubic centimetres, the precipitation being conducted in large vessels, as ordinary Winchester quart bottles. The first precipitates formed are rich in samarium, and also contain much didymium; these are followed by didymium, with some lanthanum and samarium; and the final precipitates consist almost wholly of lanthanum. By this method there are obtained three portions of hydrates, which must be again worked up separately by precipitation; the first for samarium (133), the second for didymium (127), and the third for lanthanum (125), the process of fractional precipitation being repeated on each portion fifty or a hundred times.

121. The separation of the last traces of didymium from the samarium can be accomplished only by fractional precipitation, an operation so tedious that probably few chemists will be inclined to undertake it. The second portion of hydrates, consisting chiefly of didymium, is purified from the small quantities of samarium and lanthanum by fusing with potassic nitrate, as explained above for the traces of cerium (118); to separate the lanthanum the oxalates are dissolved in warm strong nitric acid and allowed to cool, when didymic oxalate nearly free from lanthanum is obtained; after repeating several times, the last trace of lanthanum remains in the solution.

122. To separate the small quantity of didymium from the lanthanum obtained in the final precipitates with ammonia, the only method is to continue the process of fractionation; the lanthanic oxide finally obtained should be pure white, any trace of yellow showing that didymium is still present.

123. As cerite contains small quantities of the yttria earths, these must be separated from cerium, didymium, &c., by making a cold solution of the sulphates and adding finely-powdered potassic sulphate in quantity more than sufficient to saturate the solution, allowing the mixture to stand (with frequent agitation) for a few days; filtering, and washing the filtrate with a saturated solution of potassic sulphate. The filtrate contains the yttria earths, and for their complete separation it is advisable to repeat the operation with potassic sulphate three or four times. The insoluble residues, consisting of a double potassic sulphate with either cerium, didymium, or other member of this group, are boiled with sodic hydrate, filtered, well washed, re-dissolved in nitric acid, precipitated with oxalic acid, and the oxalates ignited, leaving the earths lanthana, didymia, or samaria to be finally purified as described further on.

124. The ceric oxide obtained in the manner just described was white. A considerable thickness of a strong solution did not show a trace of absorption spectrum.

The atomic weight of the metal was taken and yielded the number =141·1

The number given by BÜHRIG[*] . . . . =141·2

„ „ ROBINSON[†]. . . . . =140·2

Many older determinations[‡] range from 138 to 139.

This ceric oxide gave no orange-band spectrum in the radiant matter tube, either with or without the addition of lime.

Purification of Lanthana.

125. The lanthana obtained in the manner described above (120, 122) was more difficult to purify than ceria. Long after the lanthana appeared pure, it gave in the

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[*] Journ. prakt. Chem., (2), xii., 209.

[†] 'Chemical News,' vol. l., p. 251, Nov. 28, 1884.

[‡] *Ibid.*, vol. xlix., p. 282, June 27, 1884.

radiant matter tube a good orange-band spectrum when mixed with lime and treated as usual, although without lime it gave no spectrum.

So long as the lanthana showed the didymium absorption bands I could not be certain whether the orange-band spectrum belonged to it or to didymium, therefore the tedious process of fractionation with very weak ammonia in cold dilute solutions was repeated for some weeks. The fisrt precipitates were lanthana containing most of the didymia, whilst the final precipitates were lanthana almost if not quite free from didymia, according to the quantity originally present. After several hundred fractional precipitations repeated over and over again, a little lanthana was got which failed to show the didymium absorption bands. As the purification progressed the phosphorescent orange-band spectrum became fainter, until finally a lanthana was obtained which, mixed with lime and treated in the usual manner, gave no orange-band spectrum whatever. This lanthana was snow-white, and had an atomic weight of 138·3. **Marignac** gives for lanthana 138·6, **Brauner** 138·28, **Clève** 138·22.

Purification of Didymia.

126. The earth formerly called didymia is now known to be a mixture of didymia and samaria. The didymia which I prepared by the method described above, when mixed with lime and sulphuric acid, and tested in the radiant matter tube, gave the orange-band spectrum as brightly as I had ever seen it. It was not, however, quite free from the accompanying samaria, and systematic operations were now commenced with the object of obtaining the didymia and the samaria in a state of purity,—that is to say, in such a condition that one of them should show no orange-band spectrum at all, whilst the other should give the spectrum in its highest degree of intensity.

I did not attempt the two purifications simultaneously on the same material. One earth only was taken in hand at a time, and by repeated fractionations and the most profuse sacrifice of material, I was at last enabled to obtain a little of the desired earth quite free from admixture.

127. I took didymia first. About 1000 grms. of the earth, partially purified as described (120, 121), were dissolved in a large excess of strong nitric acid. To the nearly boiling liquid a hot saturated solution of oxalic acid was carefully added, and constantly stirred, until the precipitate, which at first rapidly disappeared, just refused to dissolve. A drop or two of nitric acid was now added to render the solution clear, and the liquid set aside to cool, when brilliant pink-coloured prisms of didymic oxalate (containing nitric acid) crystallised out. These crystals contained nearly all the didymium and samarium, whilst the mother-liquor contained the greater part of the lanthanum—reserved for the preparation of pure lanthana (125).

The crystals of didymic oxalate were ignited and again converted into nitrate, and the above-described partial crystallisation as oxalate repeated five or six times, in each case rejecting the mother-liquor as contaminated with lanthanum.

128. The final oxalates—the ultimate cumulation of the portions least soluble in nitric acid—were next converted into nitrates, and the excess of acid driven off. The anhydrous salt was dissolved in fifty times its weight of water, and fractionally precipitated by ammonia in the following manner:—A large quantity of ammonia was first prepared of the dilution (1 to 5000) used in the previous fractionation (120), and 500 c.c. of this was gradually added, with constant stirring, to Winchester quarts about three-fourths full of the dilute didymic nitrate. In about half an hour another 500 c.c. of ammonia was again added, and this operation was repeated at intervals till the Winchester quarts were full. The bulk of the samaria comes down in the first precipitates, which are filtered off and set aside for the preparation of pure samaria (133).

To the filtrate, containing didymium, with a little samarium and lanthanum, ten successive quantities of about 200 c.c. each of dilute ammonia were added to each Winchester quart at intervals of about an hour, and after violent agitation allowed to subside. The clear supernatant liquid was now poured off, evaporated to about half its bulk, and then, when cold, again poured back into the precipitate, and the operation of precipitating with dilute ammonia was likewise repeated. By this means the greater portion of the samarium present was obtained in the precipitate, whilst the didymium left in solution contained a less proportion of samarium.

129. After a time a balance seemed to be established between the affinities at work, when the earths would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them, when fractionation by ammonia could be again employed.

Samaric nitrate decomposes by heat before didymic nitrate. The nitrates were mixed with four times their weight of potassic nitrate, and the whole kept fused in a crucible till about three-fourths of the earthy nitrates were decomposed. The cooled mass was then dissolved in water, filtered, and the solution evaporated to dryness, and again submitted to fusion. This was repeated several times.

The basic nitrates insoluble in water were dissolved in nitric acid, and put through the operation of fractional precipitation with ammonia, for samaria (133), in the manner just described above (128).

130. To remove the last traces of samarium which might have survived this treatment, the solution of nitrates which had longest resisted decomposition by fusion was now mixed with excess of potassic sulphate. The precipitated double sulphates were subjected to long washing with a saturated solution of potassic sulphate, in which the samarium salt is more soluble than the didymium salt. They were then reconverted into nitrates, and the precipitation and washing with potassic sulphate repeated several times. Finally, the didymium salt was converted into oxalate, and re-crystallised many times from nitric acid, to eliminate any trace of lanthanum that might still contaminate it. Pure didymia is of a very deep chocolate-brown colour.

These proceedings are tedious enough even in their narration, but no mere words can enable the reader to realise the wearisome character of these operations when repeated day by day, month after month, on long rows of Winchester quart bottles.

131. I commenced the purification of didymia in the latter part of the year 1883, and the operations have been going on since almost daily in my laboratory. At intervals of some weeks the didymia in the then stage of purification was tested in the radiant matter tube, a little lime having previously been added to bring out the discontinuous phosphorescence. During the first month the intensity of the orange-band spectrum scarcely diminished. After this it began to fade, but the last traces of orange band were very stubborn, and not till the last few weeks could I obtain a didymia to show no trace of the orange-band spectrum ; and this result has not been accomplished without sacrifice. My 1000 grammes have dwindled away bit by bit, till now less than half a gramme represents all my store.

132. Whilst in the midst of the operations of purifying didymium and samarium I had the pleasure to receive a visit from Prof. CLÈVE, to whom we owe so much of our knowledge of the chemistry of the samarskite and cerite metals, and especially of didymium and samarium. He gave me not only most valuable information, and suggestions respecting the work I was then engaged upon, but on his return to Upsala he munificently presented me with specimens of lanthana, didymia, samaria, yttria, and erbia—specimens at that time considered to represent a state of purity. According to any chemical tests these earths would be deemed absolutely pure, but the test of the phosphorescent spectrum proved too severe a trial, and the didymia, lanthana, and samaria all showed the orange band—the lanthana faintly, the didymia more strongly, and the samaria brightest of all. A subsequent lot of "samarium-free" didymia, sent by Prof. CLÈVE, also gave a strong orange-band spectrum, though the samarium present probably did not amount to more than the one hundred thousandth part of the didymium.

Purification of Samaria.

133. The foregoing experiments left little doubt that x, the orange-band-forming body, was samarium ; the last problem was, therefore, to get this earth in a pure state. The general plan of operations was the same as I adopted in getting didymium free from samarium, only attention was now directed to the portions richest in samarium which had been formerly set aside (128, 129). On fractionation in highly dilute solutions with very weak ammonia the first precipitates are richer in samaria than the last. These first precipitates were re-converted into nitrates, and fractionation again proceeded with.

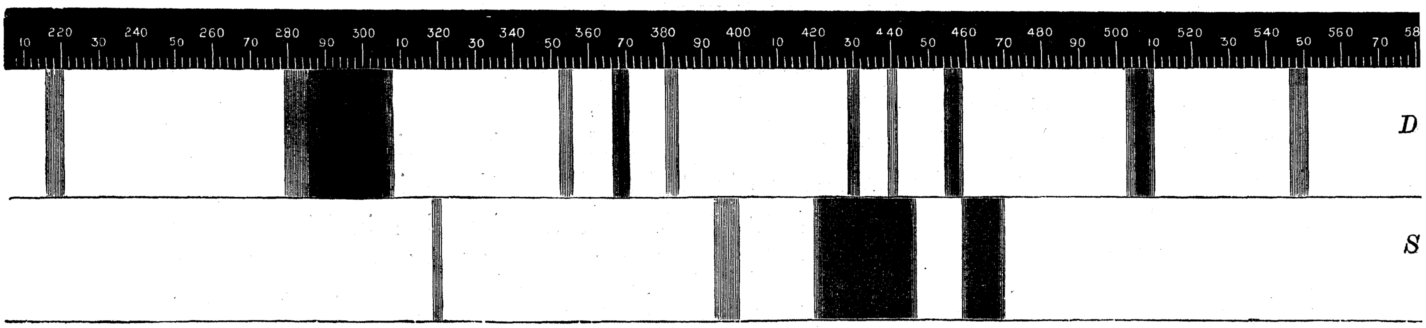
Fusion of the nitrates with potassic nitrate (129), or precipitation by, and washing with, potassic sulphate (130), are of no use in the final purification of samarium. When the object is to separate a little samarium from a large quantity of didymium, fusing the nitrates will effect the purpose, but I have not found the converse to hold good. The potassic sulphate method cannot separate the last traces of didymium from samarium, for the didymic double sulphate, not being quite insoluble, would wash out along with the first portions of the samaric salt. I have found no method better than fractionation with ammonia, and Professor CLÈVE tells me that is his experience.

Towards the end of the operations, when the samaria is getting pure, it is useful to precipitate it as a double sulphate with potassic sulphate, and wash it well for some time, to remove any traces of earths of the yttria and other groups which might have been present and become accumulated with the samaria (123).

134. During fractional precipitation with ammonia an experienced eye can judge roughly what is the preponderating earth present, by the appearance of the precipitate as it comes down. When much samaria is present, with but little didymia and lanthana, the precipitate forms immediately. When there is much didymia, and little samaria and lanthana, the precipitate forms almost as quickly as in the first case, but does not settle so rapidly. With much didymia, and a fair quantity of lanthana, the precipitate forms more slowly than before and settles sluggishly. When there is much lanthana and little didymia the precipitate takes a long time to settle, the liquid remaining opalescent for days. These peculiarities are due in great measure to the varying basicity of the elements, samarium being the least basic and lanthanum being the most basic, didymium occupying an intermediate position.

In freeing samarium from the last portions of didymium the only test available to detect the presence of the latter metal is the absorption spectrum. The best plan is to provide a strong solution of the samaric nitrate in a flask, to act as a lens, and to concentrate the light of a gas-flame by its means on to the slit of a low dispersion spectroscope. Long after the light colour of the ignited oxide shows that the didymium is getting small in quantity, its absorption bands will be so strong as almost to obliterate the fainter samarium spectrum.

Fig. 2.



135. The fractionation should be persevered in till no didymium bands are seen in the absorption spectrum. After this point is reached I prefer to keep on fractionating for some time longer, if the material will hold out, so as to make assurance doubly

sure. The colour of samaria, as pure as I have been able to prepare it, is white with the faintest possible tinge of yellow. The absorption spectrum of samarium salts is much more feeble than the spectrum of didymium salts.

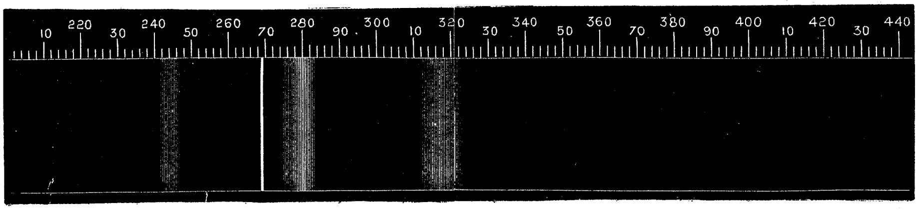
The accompanying drawing (fig. 2) shows the absorption spectra of solutions of didymic and of samaric nitrates. It will be observed that the strongest bands of the samarium absorption spectrum are almost covered by strong absorption bands of didymium. Unless, therefore, the samarium is decidedly in excess, it will be difficult for any but a very practised observer to detect its presence. Fortunately the marvellous delicacy of the phosphorescent spectrum of samarium renders any other spectrum test of little value.

136. I have already mentioned (117) that the cerite earths are supposed to contain a fifth member, which has been provisionally called Yα.[*] Not much is known respecting the properties of this earth, but from the little I can glean it would appear to become concentrated with the samarium, from which a partial separation may be effected either by continuing the operation of fractional precipitation or by taking advantage of the different solubilities of their double potassic sulphates in potassic sulphate; the potassio-samaric sulphate being almost insoluble in a saturated solution of potassic sulphate, whilst the corresponding salt of Yα is soluble in 100 to 200 volumes of the same solution. By persevering in this mode of treatment I ultimately obtained a small quantity of a white earth which gave no samarium spectrum in the radiant matter tube. Whether or no it was Yα I cannot say, as the quantity obtained was insufficient to enable me to determine its atomic weight.

The Phosphorescent Spectrum of Samarium.

137. Pure samaric sulphate by itself gives a very feeble spectrum. Some of the pure salt was heated to redness,[†] sealed in a radiant matter tube, and carefully exhausted. The coil was adjusted so as to give a powerful spark; the room was well darkened, and the eye kept shielded from extraneous light. It was difficult to hit the exact moment of exhaustion between the disappearance of gas and non-conductivity, but by careful watching at the spectroscope a point was reached at which the

Fig. 3.



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[*] Marignac, 'Comptes Rendus,' vol. 90, p. 899; 'Chemical News,' vol. 41, p. 250.

[†] Samaric sulphate is not decomposed at the temperature employed.

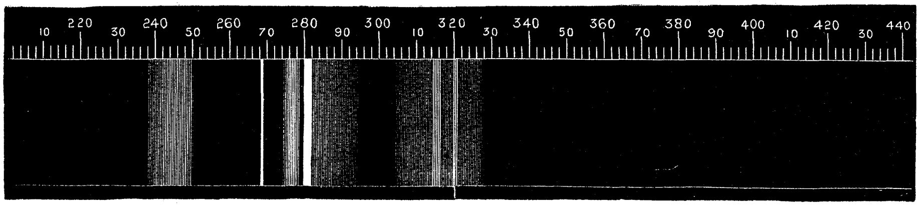
phosphorescence appeared. The spectrum consists of a faint band in the red, then a sharp orange line (146, 165), next a wide ill-defined orange band, and finally an equally ill-defined green band. The appearance is shown in fig. 3.

138. When, however the samaria is mixed with lime (114) before examination in the radiant matter tube, the change is very striking, and the spectrum is, if anything, more beautiful than that of yttrium. The bands are not so numerous, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, which require care to bring them out, the spectrum is seen to consist of three bright bands,—red, orange, and green,—nearly equidistant, the orange being the brightest. With a narrower slit the orange and green bands are seen to be double, and on closer examination faint wings are seen, like shadows to the orange and green bands. In this spectrum the sharp orange-coloured line (137) of pure samaric sulphate is absent.

139. The bands are best seen in a spectroscope of low dispersion, and with not too narrow a slit. In appearance they are more analogous to the absorption bands seen in solutions of didymium than to the lines given by spark spectra. Examined with a high magnifying power all appearance of sharpness generally disappears : the scale measurements given below must therefore be looked upon as approximate only; the centre of each band may be taken as accurately determined within the unavoidable errors of experiment, but it is impossible to define their edges with much precision.

140. The accompanying cut (fig. 4) gives as good an idea of the spectrum of samarium-calcium as is possible in black and white. The numbers along the top are the squared reciprocals of wave-lengths, and are on the same scale as the diagram of the yttrium spectrum (71) given in my Bakerian Lecture already quoted. The phosphorescing mixture in the tube consisted of 20 parts of pure samaria and 80 parts of lime. They were converted into nitrates in a platinum capsule, and then decomposed by excess of sulphuric acid and ignited at a dull red heat. If sulphuric acid is added in the first instance there is a difficulty in getting the earths completely converted.

Fig. 4.



The least refrangible band seen is a very faint red, which extends from $\frac{1}{\lambda^2}$ 2310 to 2400. Here a much stronger red band begins extending to 2494. The first component of the bright orange band begins at 2739 and ends at 2762. Between 2762 and 2798 is a dark interval, and then the second component of the orange band is seen extending from 2798 to 2818. This band is stronger and more sharply defined than the preceding band. A faint yellow wing extends from the second orange band to 2942. There is now an intensely black interval reaching to 3025; here a faint yellowish-green light is seen extending to 3149, where the green band commences and extends to 3164. Here a fainter green wing begins, and extends to 3270. On this wing a very narrow faint green band is seen, having its centre at 3190. There is then another dark space, after which three ill-defined blue and violet bands are seen, too faint to measure accurately.

141. Preliminary experiments (114) had shown me that lime was one of the best materials to mix with samaria in order to bring out its phosphorescent spectrum, but it was by no means the only body which would have the desired effect. More accurate observations were now taken with pure materials mixed together in definite quantities. The bodies employed were those enumerated in par. 113. Of these the following induced no phosphorescence:—zirconium, cerium, didymium, copper, silver, manganese, and tin; silicic, titanic, tungstic, molybdic, niobic, and tantalic acids.

142. The other substances which I tried caused the samarium to give good phosphorescence with a discontinuous spectrum. There is a general resemblance between these spectra, but nearly all of them differ one from another in details. In the following descriptions I will take the calcium-samarium spectrum (140) as the standard of comparison:—

Strontium and barium, when mixed with samarium, give almost identical spectra; the red band is similar to the one produced by calcium, but the orange bands have become a blurred orange space, with outline ill-defined on the side towards the red, and sharper at the more refrangible side. There is no trace of division in the orange space; but the green, which with calcium is narrow and single, becomes with barium and strontium a well-defined luminous double green band, with a sharp black separating interval.

Beryllium and samarium give a very faint phosphorescent spectrum, consisting of a red, orange, and green band only; the green occupying the position of the second green band given by calcium-samarium.

143. Thorium and samarium give a very similar spectrum to the one produced by barium or strontium with samarium, a slight difference being observable in the orange, which shows signs of separation into two components.

Thorium, as oxide or sulphate, by itself gives no phosphorescence (26, 28), and in fact, as I have already shown, renders the vacuum tube non-conducting;* samaria

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* "This earth is, however, remarkable for its very strong attraction for the residual gas in the vacuum tube. On putting thorina in a tube furnished with well-insulated poles, whose ends are about a millimetre apart in the centre, and heating strongly during exhaustion, the earth, on cooling, absorbs the residual gas with such avidity that the tube becomes non-conducting, the spark preferring to pass several inches in air rather than strike across the space of a millimetre separating the two poles."—Proc. Roy. Soc., No. 213, 1881, Vol. XXXII., p. 209.

likewise gives scarcely any phosphorescence (137). It is, therefore, somewhat remarkable that a mixture of these two bodies should bring out the samarium spectrum so brilliantly.

Magnesium and samarium give the red band and second orange band sharply; the first orange is, however, obliterated, and its place occupied by a faint, broad, ill-defined band, extending to the orange band. The green band is very wide, faint, and ill-defined.

Zinc and samarium give the red band as usual, but there is only one orange band, which is sharp, and occupies the position of the interval between these bands in the calcium and samarium spectrum. The green band is widened out, and occupies the position of the second green band of the thorium-samarium spectrum.

The cadmium-samarium spectrum is similar to that of zinc-samarium, only the green band is still wider, and extends further towards the red end.

144. Lead with samarium gives a very brilliant spectrum. The red is clear and sharp, and has a narrow faint wing on each side. The orange is one wide band, with no trace of division, whilst the green is sharp and duplicated as in the thorium-samarium spectrum, to which, indeed, it bears a great resemblance. The centres of the green bands are at $\frac{1}{\lambda^2}$ 3133 and 3199.

Lanthanum and samarium phosphoresce brightly, and give a very sharp spectrum consisting of three bands, closely resembling the zinc-samarium spectrum; the red, however, not being so bright as the other two bands. On the contrary, cerium or didymium mixed with samarium gives no phosphorescence.

Aluminium and samarium give a spectrum resembling the corresponding calcium one as to the red and double orange, but having a very broad, somewhat faint, green band, with a black division in the middle occupying the position of the bright green band of calcium-samarium.

Bismuth and samarium gave a somewhat faint spectrum, almost identical with the lanthanum-, zinc-, cadmium-, and glucinum-samarium spectrum.

The antimony-samarium spectrum is almost identical with that with bismuth, the spectrum being, however, much fainter.

145. The samarium spectra, modified by other metals as above described, may be divided into three groups. The first group comprises the spectra given when glucinum, magnesium, zinc, cadmium, lanthanum, bismuth, or antimony is mixed with the samarium. It consists simply of three coloured bands, red, orange, and green; as a typical illustration I will select the lanthanum-samarium spectrum (fig. 5). The centres of the bands are—red 2429, orange 2808, and green 3177.

The second type of spectrum gives a single red and orange and a double green band. This is produced when barium, strontium, thorium, or lead are mixed with samarium. The lead-samarium spectrum (fig. 6) illustrates this type. The centres of the bands of this spectrum are—red 2437, orange 2830, green 3133 and 3199.

The third kind of spectrum is given by calcium mixed with samarium. Here the red and green are single, and the orange double. Aluminium would also fall into this class were it not that the broad ill-defined green band is also doubled. The calcium-samarium spectrum, already illustrated in fig. 4 (140), is a good illustration of this type.

Fig. 5.

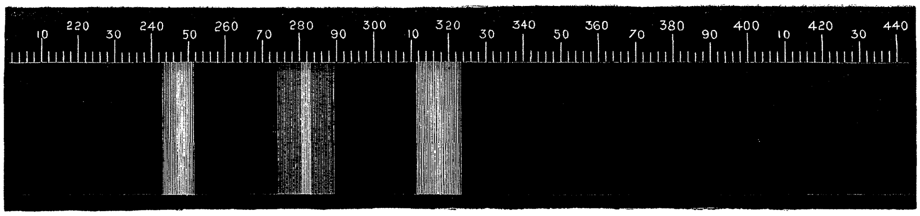
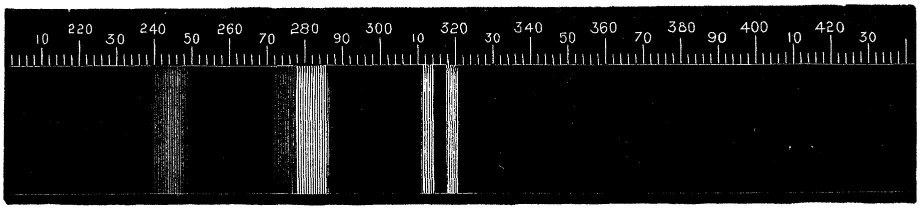


Fig. 6.



Mixed Samarium and Yttrium Spectra.

146. It was interesting to ascertain what spectrum a mixture of samarium and yttrium would give. A mixture of 90 parts of samaria to 10 of yttria was treated with sulphuric acid and then ignited, and afterwards examined in the radiant matter tube. The result was as remarkable as it was unexpected. Scarcely a trace of the yttrium spectrum could be detected. The powder phosphoresced with moderate intensity, but the spectrum was almost the facsimile of that given by pure samaric sulphate (137, fig. 3), except that the sharp orange line, which in the spectrum of pure samaric sulphate is only just visible, had gained sufficiently in intensity to be measurable, and was found to lie at 2693. I next tried a mixture of samaria 80, and yttria 20. The spectrum was identical with the one last observed, with one striking difference—the 2693 line now shines out with great brilliancy of a fine orange-red colour, as sharp as a gas line, and so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture.

The next tube experimented with contained 70 parts of samaria and 30 parts of yttria. The spectrum was identical with the one last observed. The sharp orange line was present in full intensity.

147. Mixtures were now made of samaria 60, yttria 40; samaria 60·63, yttria 39·37 (equivalent proportions of the two earths); in this last a slight division could be

detected in the green band. The following experiments were continued; mixtures were prepared in the following proportions:—

Samaria.	Yttria.
58	42
56	44
54	46
53	47
52	48
51	49
50	50
49	51
48	52
47	53
46	54
45	55

The results were almost identical with those yielded by the previous mixtures. The green band gradually condensed into two bands at $\frac{1}{\lambda^2}$ 3133 and 3199 as the proportion of yttria increased; the first green band was stronger than the other, and the wide orange band began to show signs of a wing on the side next the green. At this stage the spectrum nearly resembled the lead-samarium spectrum (145, fig. 6). Very little of the yttria spectrum could be detected, and the brilliant orange line stood out sharply in the whole series.

In the next mixture—samaria 44, yttria 56—a faint band $\left(\frac{1}{\lambda^2}\ 3038\right)$, was visible by the side of the two green bands, in the position occupied by the yellow band of yttria.

148. The experiments were continued, and the following mixtures were made and and carefully mapped:—

Samaria.	Yttria.
43	57
42	58
41	59
40	60
39	61

The faint line first observed in samaria 44, yttria 56, gradually got stronger, and there were also signs of a double green band in about the position occupied by the yttrium green.

149. The change which had been rapidly coming over the spectra since samaria 43, yttria 57, was now nearly accomplished, and in the next trial mixture—samaria 35,

yttria 65—the only indication that could now be found of the samarium spectrum was seen in the two faint green bands next to the citron line of yttria, a faint yellow band, and the new orange line, which shone out as brightly and sharply as ever.

The series was continued :—

Samaria.	Yttria.
30	70
25	75
20	80
10	90
5	95

In each case a careful map of the spectrum was taken on the $\frac{1}{\lambda^2}$ scale, and each spectrum was found to be practically identical. Slight differences in the relative intensities of some of the bands were observed; but the general character of the spectrum was unaltered. The yttria spectrum now shone forth with scarcely any band of samaria, except that, standing out beyond the other bands in sharpness and brilliancy, the 2693 line was present in all.

150. It will be remarked that a sudden change occurs between the two mixtures, samaria 45, yttria 55, and samaria 35, yttria 65; on one side the spectrum pertains to that of samaria, whilst on the other side the spectrum is that of yttria, the new orange line running equally across them all.

Fig. 7.

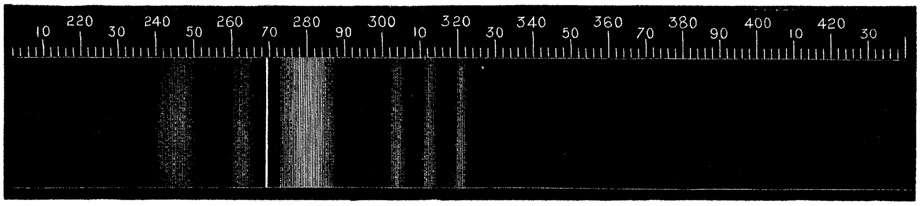
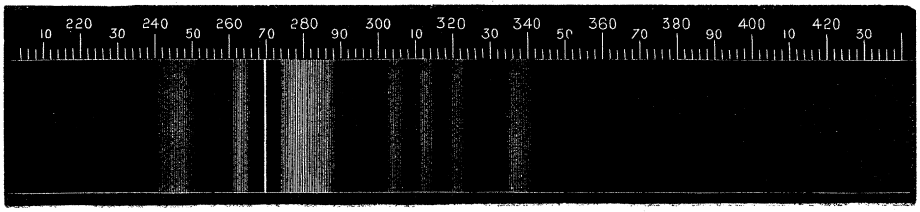


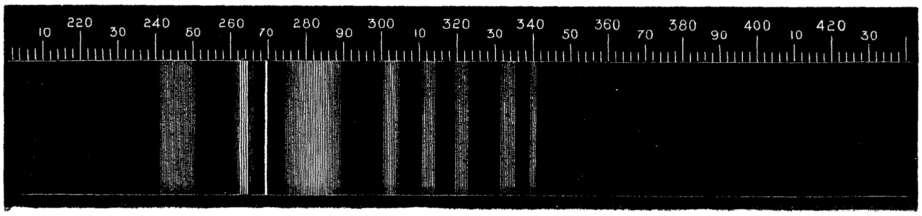
Fig. 8.



151. The diagrams of some of these intermediate spectra shown in the accompanying figures illustrate how sudden is the transformation from the samarium to the yttrium spectrum. Fig. 7 is the spectrum of a mixture of 44 parts samaria and 56 parts yttria, and except for the increased strength of the orange line, and a faint trace of the red and yellow yttria bands, it is the pure samarium spectrum. Fig. 8 is the

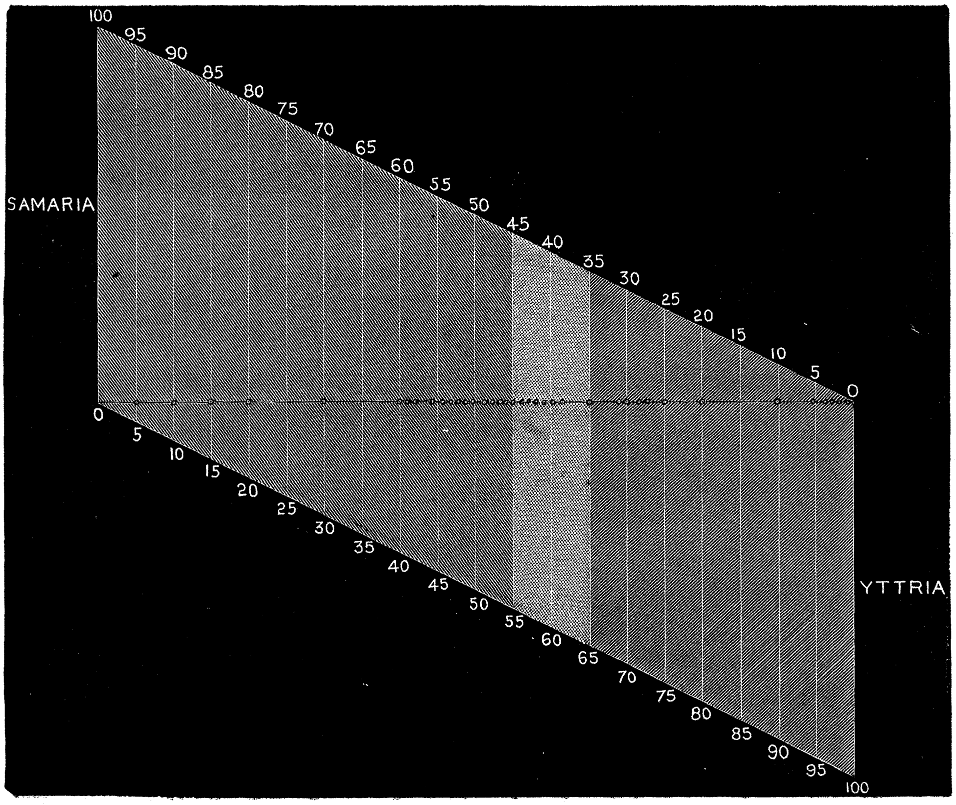
spectrum of 42 samaria and 58 yttria, and is built up of some of the component bands of the spectrum of each earth: whilst in fig. 9, the spectrum of 39 samaria and 61 yttria is seen to be almost the yttria spectrum.

Fig. 9.



152. I have already shown (86) that one part of yttrium can be detected spectroscopically in the presence of a million parts of calcium, and the reaction is almost as sensitive if other earths are taken instead of lime. Again, the spectrum test for samarium is, if possible, even more delicate (156 to 163), one part being detectible when mixed with more than two million parts of calcium.

Fig. 10.



153. The accompanying diagram (fig. 10) shows at a glance the remarkable effect these two earths have of masking each other's spectrum reactions. The ordinates above the horizontal zero line represent the percentages of samaria in the mixtures examined, and the lower ordinates show the percentages of yttria present. The dots

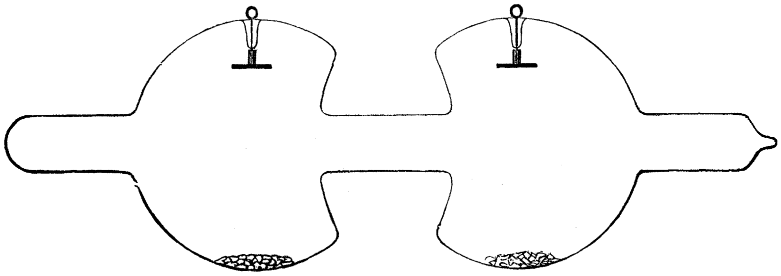
on the horizontal line show the actual mixtures experimented with (146 to 149). The part to the left covers the mixtures showing a preponderance of the samarium spectrum, and the right-hand portion shows the mixtures which give preponderance to the yttrium spectrum only. The intermediate portion covers the narrow borderland in which the fainter mixed spectra were observed.

In no mixture does the resulting spectrum contain the complete spectrum of either earth, many bands of each being suppressed.

154. It was of interest to ascertain whether the orange line 2693 could be evoked by mechanically forming a mixture which, when prepared chemically, gave the line strongly.

A radiant matter tube was made in the form of a double bulb, as shown in Fig. 11.

Fig. 11.



In one half was introduced ignited samaric sulphate, and in the other half the same weight of yttric sulphate, each being finely powdered. The tube was well exhausted and the powders separately examined with the spectroscope. Each gave its characteristic spectrum (72, 137). The double bulb was now sealed off, and the powders well mixed by violent agitation. On careful examination it was seen that the spectrum shown by the mixture was simply that of the two components superposed, and had no resemblance to the spectrum shown by a similar mixture prepared by solution and chemical action (fig. 13.)

The Action of Calcium on the Samarium-Yttrium Spectrum.

155. The addition of calcium to mixtures of samarium and yttrium has the effect of greatly developing the samarium spectrum, and, *pari passu*, of impairing the sharpness of the bands of the yttria spectrum. This exaltation of the samarium bands is not, however, effected without a corresponding loss. The brilliantly sharp orange line 2693 entirely disappears.

Fig. 12 is a drawing of the spectrum given by a mixture of equal parts of samaria, yttria, and lime. On comparing it with fig. 13, which represents the spectrum given by the same mixture without the lime, it will be seen that the action is as might have been anticipated from previous experiments. The lime has divided the samarium orange band and strengthened the red, whilst it has increased the brilliancy of the yttrium citron and green, and brought out the blue and violet bands.

Fig. 14 is a representation of the spectrum given by a mixture of samaria 2, yttria 54, and lime 44. Even with this large amount of yttria present the samarium spectrum greatly overpowers that of yttrium. Without the lime very little samarium would be visible in this mixture (149).

Fig. 12.

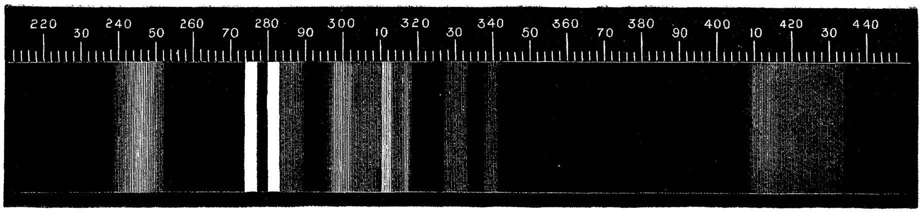


Fig. 13.

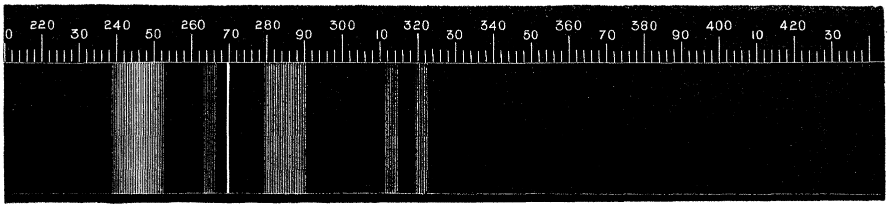
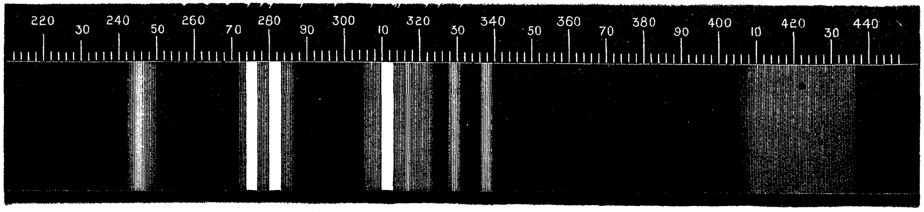


Fig. 14.



The Delicacy of the Spectrum Test for Samarium.

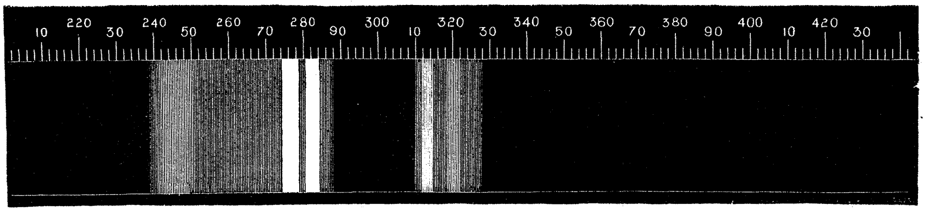
156. The foregoing observations had prepared me for the exceeding delicacy of this spectroscopic test for samarium. Experiments were now commenced with the object of getting some approach to a quantitative estimate of how small a quantity of samarium could be detected.

A solution of specially purified calcic nitrate (79) which was found to contain neither yttrium nor samarium by the radiant matter test, was standardised, so that one part of calcium was contained in 50 parts of solution.

157. A standard solution of samaric nitrate was made containing 1 part of samarium in 100,000 parts of solution.

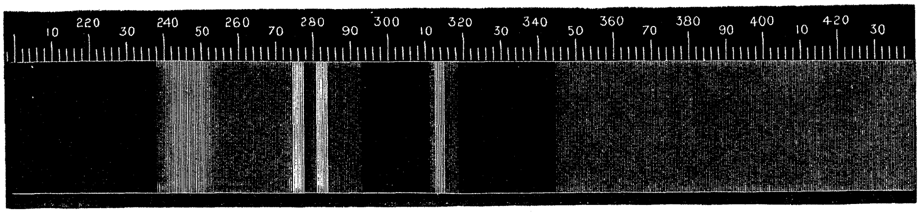
These solutions were mixed in the proportion of 1 part samarium to 100 parts of calcium. The spectrum (fig. 15) was very brilliant, and but little inferior in sharpness to the spectrum given by a 50 per cent. mixture.

Fig. 15.



158. A mixture was now prepared containing 1 part of samarium to 1000 parts of calcium. Very little difference could be detected between the spectrum of this mixture and that of the last. The bands were, however, a little less sharp. Fig. 16 shows the appearance of this spectrum.

Fig. 16.



159. A mixture containing 1 part of samarium to 10,000 parts of calcium. The resulting spectrum is shown in fig. 17. The bands are now getting fainter, the second green band is fading out, and the continuous spectrum of calcic sulphate is getting brighter.

Fig. 17.

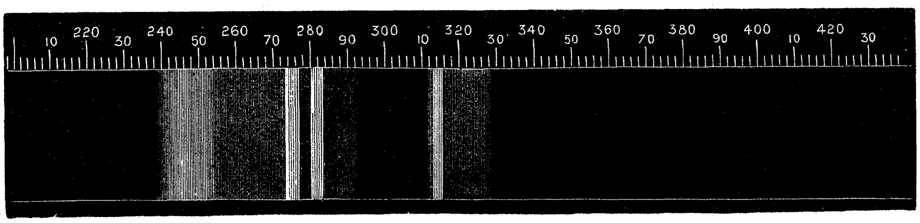
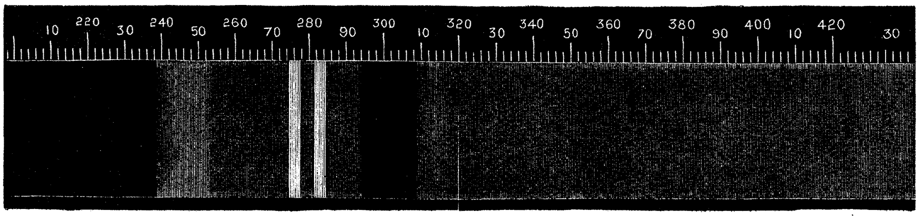


Fig. 18.

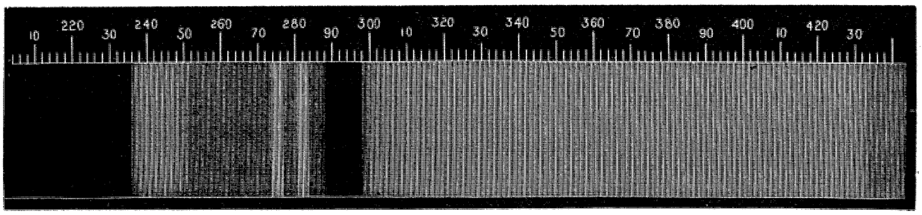


160. The next mixture tried contained 1 part of samarium in 100,000 parts of calcium. The appearance of the spectrum is shown in fig. 18. Here the green is

almost gone, being overshadowed by the continuous spectrum of calcium which has spread over it. The red band has likewise almost disappeared in the greater brightness of the continuous red of the calcic spectrum. The double orange band is still very prominent, and the black space, 2942, between it and the green is very marked.

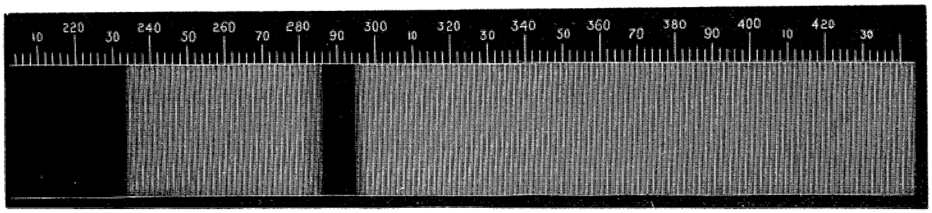
161. The next mixture, 1 part of samarium to 500,000 parts of calcium, gives a spectrum which is fainter than the last, but the orange bands are still distinctly visible. The black space between the yellow and green is strongly marked, but narrower than before. Fig. 19 shows the appearance of this spectrum.

Fig. 19.



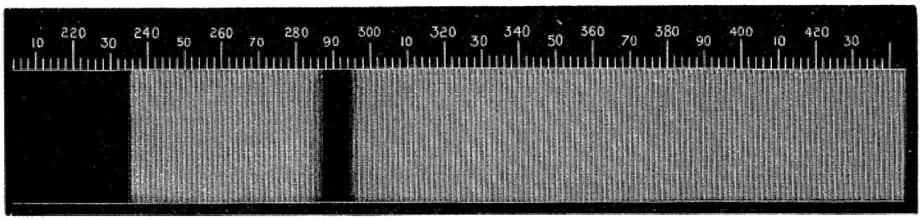
162. A mixture of 1 part of samarium in 1,000,000 parts of calcium was next subjected to experiment. In this the samarium spectrum is very feeble, and the orange bands are only to be seen with difficulty. Now the most striking characteristic of this spectrum is the black space which still cuts out the greater portion of the yellow. Fig. 20 represents this spectrum.

Fig. 20.



163. A mixture of one of samarium in 2,500,000 parts of calcium was now taken.

Fig. 21.



In the spectrum shown by this mixture the bands of samarium have entirely gone, and its presence now is apparent only by the darkening in the yellow portion of what otherwise would be a continuous spectrum. Fig. 21 shows this appearance.

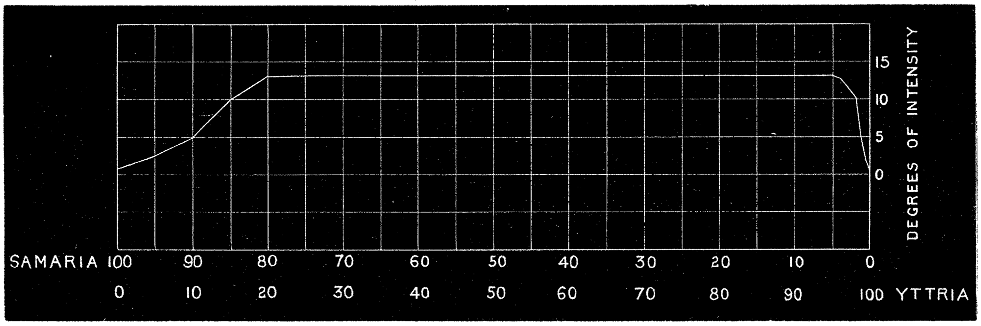
164. Finally the calcium spectrum by itself was examined. It is continuous, with no break, lines, or bands in it.

The Anomalous Line $\frac{1}{\lambda^2}$ 2693.

165. On several occasions I have spoken of an orange line, 2693, which by its brilliancy and sharpness is a prominent object in most of the samarium-yttrium spectra. With samaric sulphate it is exceedingly faint. With samaria containing 5 per cent. of yttria it is very little brighter; with 10 per cent. of yttria it gains a little; with 15 per cent. it is brighter still, and with a mixture of 80 parts samaria and 20 parts yttria it is at its maximum intensity. It continues to be the most striking feature in the spectra of the various mixtures of samaria and yttria until the proportion becomes samaria 3, yttria 97, when it begins to get less bright, and only when pure yttria is reached does it altogether vanish.

The accompanying diagram (fig. 22) shows the rise and fall in intensity of this bright line, with the proportions of samaria and yttria experimented on.

Fig. 22.



166. It is noteworthy that so long as this bright line is a component of the spectrum, the other bands manifest decidedly less intensity than they do in other phosphorescent spectra where this line is absent. Many of the bands usually present in the samaria and yttria spectra are also suppressed. The profound modification in the spectra of samaria and yttria developed by their mixture is, I believe, without precedent in spectrum analysis. The molecules of each earth, samaria and yttria, which separately are capable of vibrating rhythmically and of giving a characteristic phosphorescent spectrum, when mixed yield a spectrum approaching in character that of samaria or of yttria, according as one or other earth preponderates, and produce the dominant line 2693.

167. In this and the former paper on Radiant Matter Spectroscopy, much stress has been laid on the sensitiveness of the Radiant Matter test for indicating the

presence of samarium and yttrium; but it might be argued, from the anomalies that arise when *both* these elements occur together, that in reality the Radiant Matter test, however delicate, is one not to be depended upon. For instance, it might reasonably be asked what inference is to be drawn in the case of certain minerals treated with sulphuric acid and tested in the vacuum tube, and found to give only a feeble spectrum? Does this prove the absence of all but traces of either samarium or yttrium, or does it show the presence of both these earths in considerable quantity? The answer is simple. In spite of the perplexing anomalies that have come to light, and are described in this paper, regarding the influence of these two phosphorescing earths on each other, no single instance has occurred during the work connected with this subject in which, with the experience now gained, brilliant phosphorescence and a characteristic spectrum could not be evolved from any mixture containing both or either of the earths samaria and yttria. If, after treatment with sulphuric acid and ignition, the earthy mixture gives a pure spectrum of either yttria or samaria, and the line 2693 is absent, it is pretty safe to assume that the particular earth indicated is alone present. If, however, the spectrum is not quite characteristic, or the anomalous line 2693 is present, it is not sufficient to test the unknown mineral or mixture direct in the vacuum tube. It must first be treated chemically to separate the samaria and yttria (123, 133), and lime must be added before testing in the radiant matter tube (138), when the spectrum immediately makes its appearance if either of these earths be present in the smallest quantity. Although I say lime is to be added, many other substances perform the same office of eliciting the spectrum, such as baryta, lead, &c. (142—145); but my chief experience has been with lime, and I have always found it to give uniform results under varied conditions.

One important lesson taught by the many anomalies unearthed in these researches is, that inferences drawn from spectrum analysis *per se* are liable to grave doubt, unless at every step the spectroscopist goes hand in hand with the chemist. Spectroscopy may give valuable indications, but chemistry must after all be the court of final appeal.

168. Chemistry, however, by itself would have been helpless to solve the difficulties had it not been possible to appeal at every step to the radiant matter tube and to the spectroscope. The problems to be solved are so new as to be entirely outside the experience of laboratory work. A double orange-coloured band shows itself in a faint emission spectrum obtained under novel circumstances. On further examination the band, or one not far from it, is seen to occur in minerals of very divergent kinds and apparently irrespective of their chemical constitution or locality, as well as in laboratory reagents and chemicals of assured purity. This band is sometimes accompanied by bands in other parts of the spectrum, and occasionally shifts its place to the right or to the left. Frequently the orange band disappears and a citron-coloured band takes its place. Chemical research continued for a longer time than most chemical researches require fails to throw any light on the subject. These being the conditions

of the problem, the very last explanation likely to occur to the enquirer would be that these elusive shifting bands were due to the presence of two elements almost universally distributed, and that these two elements should be yttrium and samarium,—yttrium one of the rarest of known elements, and samarium, almost unknown at the time its spectrum reaction was first discerned.

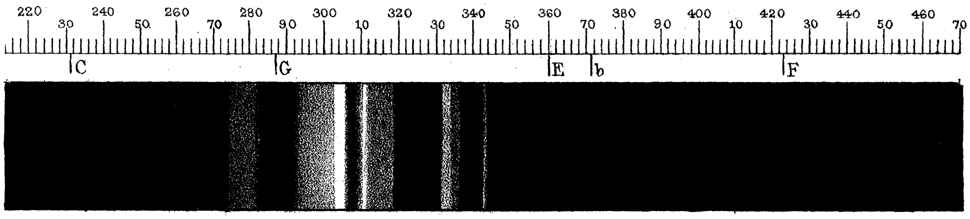
DESCRIPTION OF THE COLOURED LITHOGRAPH.

PLATE 75.

The uppermost spectrum is that of yttric sulphate in the radiant matter tube. It is copied in colours from the author's Bakerian Lecture already quoted, and is placed at the head of the coloured spectra for convenience of comparison.

The other spectra are coloured copies of the illustrations in the text, and are designated by the same numbers.

The
Yttria
Spectrum.



Vide Phil. Trans.
Vol. 17. 1883.
(p. 891.)

Sm

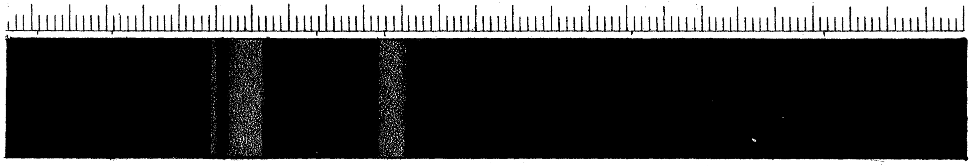


Fig. 3.

Sm 50
La 50

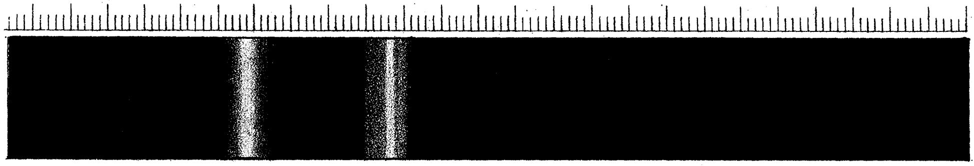


Fig. 5.

Sm 50
Pb 50

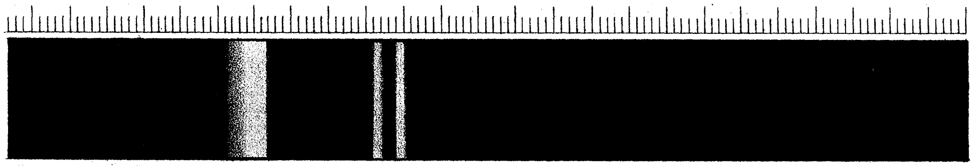


Fig. 6.

Sm 44
Yt 56

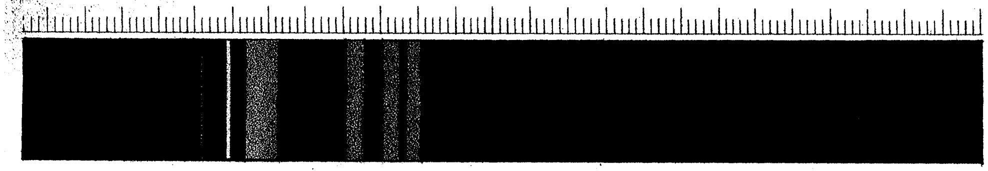


Fig. 7.

Sm 42
Yt 58

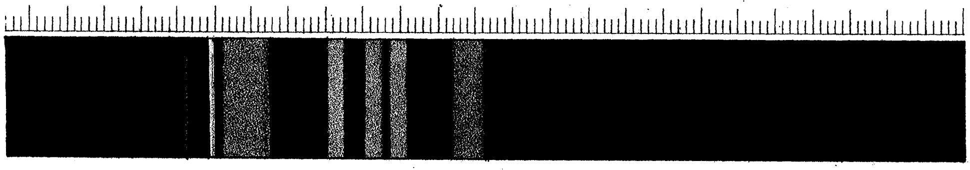


Fig. 8.

Sm 39
Yt 61

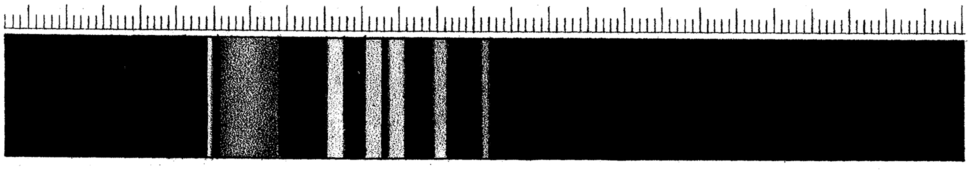


Fig. 9.

Sm 20
Ca 80

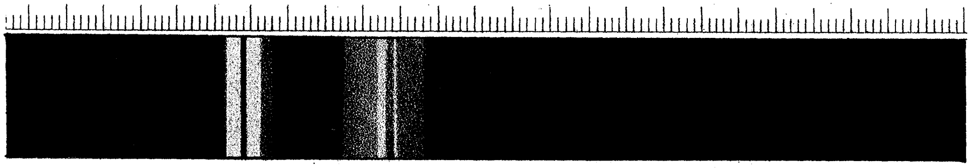


Fig. 4.

Sm 1
Ca 100,000

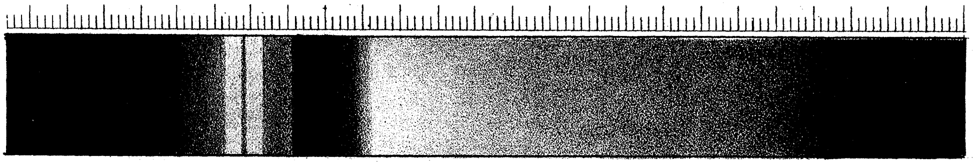


Fig. 18.

Sm 1
Ca 2,500,000

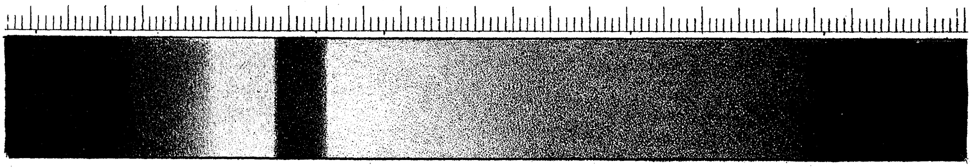
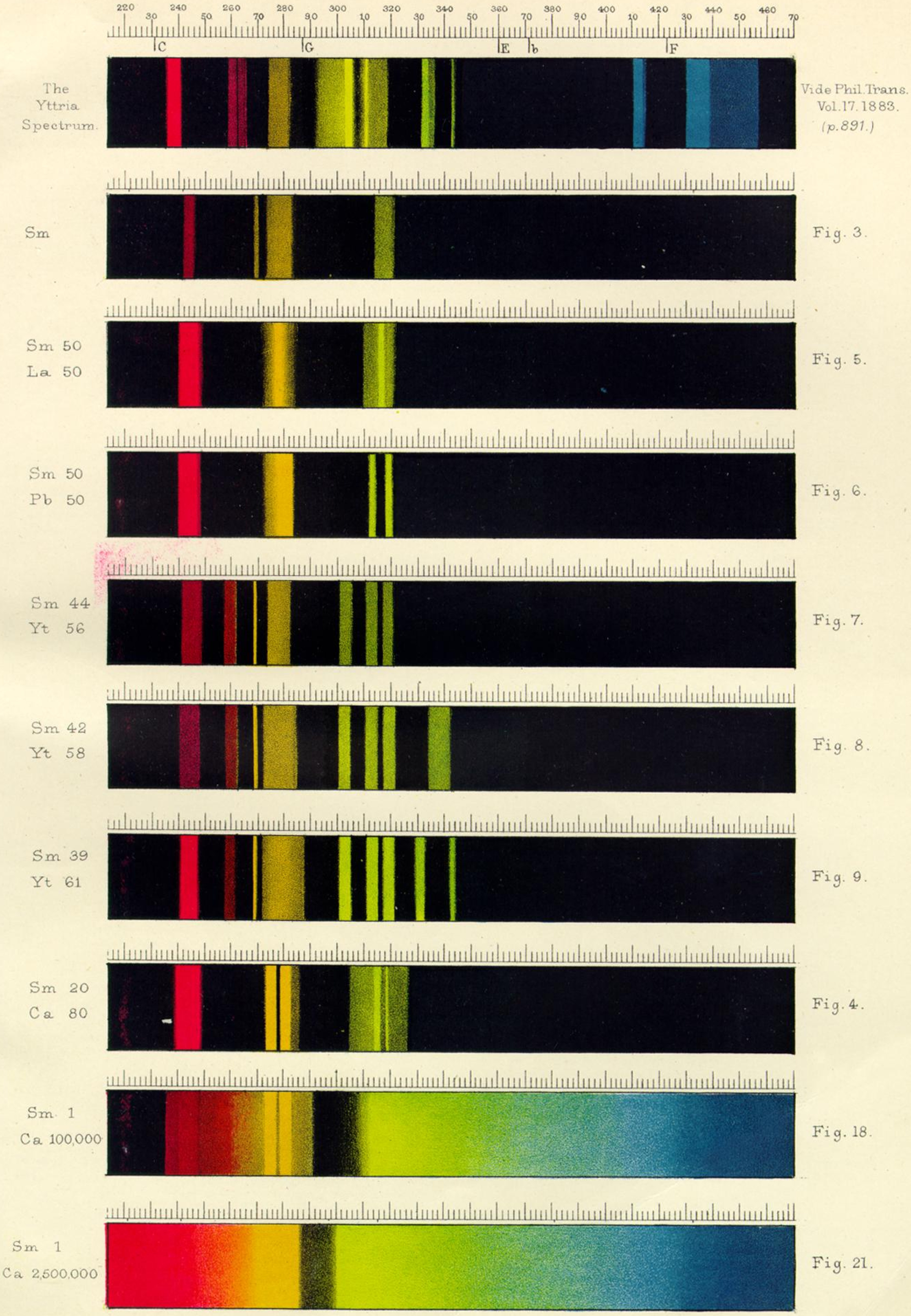


Fig. 21.

West, Newman & Co. lith.



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