## XXVII. The Bakerian Lecture.—*On Radiant Matter Spectroscopy: The Detection and wide Distribution of Yttrium.*

### *By* William Crookes, *F.R.S.*

### *Introduction.*

1. In March, 1881, I sent to the Royal Society a preliminary notice of some results I had obtained when working on the molecular discharge in high vacua.* When the spark from a good induction coil traverses a tube having a flat aluminium pole at each end, the appearance changes according to the degree of exhaustion. Supposing atmospheric air to be the gas under exhaustion, at a pressure of about 7 millims. a narrow black space is seen to separate the luminous glow and the aluminium pole connected with the negative pole of the induction coil. As the exhaustion proceeds this dark space increases in thickness, until, at a pressure of about 0·02 millim. (between 20 and 30 M.)†, the dark space has swollen out till it nearly fills the tube. The luminous cloud showing the presence of residual gas has almost disappeared, and the molecular discharge from the negative pole begins to excite phosphorescence on the glass where it strikes the side. There is great difference in the degree of exhaustion at which various substances begin to phosphoresce. Some refuse to glow until the exhaustion is so great that the vacuum is nearly non-conducting, whilst others begin to become luminous when the gauge is 5 or 10 millims. below the barometric level. The majority of bodies, however, do not phosphoresce till they are well within the negative dark space. This phosphorogenic phenomenon is at its maximum at about 1 M., and, unless otherwise stated, the experiments now about to be described were all tried at this high degree of exhaustion.

Under the influence of this discharge, which I have ventured to call radiant matter, a large number of substances emit phosphorescent light, some faintly and others with great intensity. On examining the emitted light in the spectroscope most bodies give a faint continuous spectrum, with a more or less decided concentration in one part of the spectrum, the superficial colour of the phosphorescing substance being governed by this preponderating emission in one or other part of the spectrum.

Sometimes, but more rarely, the spectrum of the phosphorescent light is discontinuous, and it is to bodies manifesting this phenomenon that my attention has been

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* Proceedings of the Royal Society, No. 213, 1881.

† M. = one-millionth of an atmosphere.

specially directed for some years past, considerable interest attaching to a solid body whose molecules vibrate in a few directions only, giving rise to spectrum lines or bands on a dark background.

## The citron band spectrum.

2. For a long time past I have been haunted by a bright citron-coloured band or line appearing in these phosphorescent spectra, sometimes as a sharp line, at others as a broader nebulous band, but having always a characteristic appearance and occurring uniformly in the same spot. This band I first saw in the summer of 1879, and from that date down to a comparatively short time ago all my efforts to clear up the mystery proved vain. By chemical means it was not difficult to effect a partial separation of a certain mineral or earthy body into two parts, one giving little or no citron band, the other giving one stronger than the original band; and by again treating this latter portion by appropriate chemical means, the citron band-forming body could frequently be still more concentrated; but further than this for a long time it seemed impossible to go. I soon came to the conclusion that the substance I was in search of was an earth, but on attempting to determine its chemical properties I was baffled. A more Proteus-like substance a chemist never had to deal with. In my preliminary note, above referred to, speaking of the possibility that some of these spectrum-forming bodies might be new chemical elements, I said—" The chemist must be on his guard against certain pitfalls which catch the unwary. I allude to the profound modification which the presence of fluorine, phosphorus, boron, &c., causes in the chemical reactions of many elements, and to the interfering action of a large quantity of one body on the chemical properties of another which may be present in small quantities."

3. This warning was not unnecessary. No Will-o'-the-Wisp ever led the unwary traveller into so many pitfalls and sloughs of despond as the hunt for this phantom band has entrapped me. I have started with a large quantity of substance which, from preliminary observations, promised to be a rich mine of the desired body, and have worked it up chemically to a certain point, when the citron band vanished, and could not be again detected in either precipitate or filtrate. Half-a-dozen times in the last four years the research has been given up as hopeless, and only a feeling of humiliation at the thought of a chemist being beaten by any number of anomalies made me renew each time the attack. Likewise, the tedious character of the research made a long continuance of failures very disheartening. To perform a spectrum test, the body under examination must be put in a tube and exhausted to a very high point before the spectroscope can be brought to bear on it. Instead of a few minutes, many hours are occupied in each operation, and the tentative gropings in the dark, pre-eminently characteristic of this kind of research, have to be extended over a long period of time.

4. I soon found that the best way to bring out the band was 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 (10). The anhydrous sulphate thus left frequently showed the citron band in the radiant matter tube, when before this treatment the original substance showed nothing (75).

## Examination of calcium compounds.

5. My first idea was that the band might be due to a compound of lime. Much chemical evidence tended to support this view. I have already explained that the chemical extraction was rendered very difficult by the fact of the citron band so frequently turning up both in the precipitate and the filtrate. By neglecting the portion showing least citron band, and separating all the elements present which gave little or none, I could generally concentrate the citron band into a solution which —according to our present knowledge of analytical chemistry—should contain little else than the earths, alkaline earths, and alkalies. Ammonia added to this solution would precipitate an earth (11, 14), and in the filtrate oxalic acid would precipitate an insoluble oxalate (7, 13).

The citron band hovered between these two precipitates, being sometimes stronger in one and sometimes in the other. It was also to be detected, but more faintly, in the residue left after evaporating to dryness and igniting the filtrate from the oxalate.

I frequently obtained no precipitate with ammonia, and then the oxalate gave the band brilliantly ; and occasionally the ammonia precipitate when formed gave little or no citron band. I was, however, generally sure to find it in the insoluble oxalate, and sometimes it was very brilliant, being accompanied by two bright green bands and a fainter red band.

6. At this time one of the minerals which showed the citron band most strongly was a phosphorescent apatite from Ireland ; and knowing the difficulties of separating the last traces of phosphoric acid from the earths, I explained the foregoing facts by the presence of small quantities of phosphoric acid, which gave rise to the ammonia precipitate ; the bulk of the citron body not being precipitated by ammonia, but coming down as oxalate ; whilst a little of this oxalate would remain dissolved in the ammoniacal salts present, and so appear with the alkalies.

I tested this hypothesis in every imaginable way, by mixing small quantities of phosphoric acid with salts of lime and other earths, in the endeavour to imitate the conditions occurring in the native minerals, and so educe the citron band ; but I was unable to get any precipitate giving the citron band when I started with materials which did not originally give it.

7. A sufficient quantity of precipitated oxalate (5) having in course of time been accumulated, I attempted its purification. It was ignited, dissolved in dilute hydro-chloric acid, and rendered slightly alkaline with ammonia and ammonic sulphide. The liquid was boiled to a small bulk, keeping it alkaline, and was then set aside in

a warm place : a slight flocculent precipitate formed. This was filtered, and the filtrate re-concentrated. The clear strong solution should now contain nothing but barium, strontium, and calcium, with traces of elements from previous groups which might be soluble in the precipitants employed or in the ammoniacal salts present (for we know that the word *insoluble* applied to a precipitate is not an absolute term, and in minute analysis allowance must be made not only for the slight solubility of precipitates in the reagents present, but also for the power possessed by most precipitates of carrying down with them traces of soluble metallic salts from solution). Besides these, it was possible that a hitherto unrecognised element might be present, to which the citron band was due. By the ordinary process of analysis I could, however, only detect the presence of calcium and strontium.

8. The concentrated ammoniacal solution was added to an excess of a boiling solution of ammonic sulphate, and the whole was set aside for twenty-four hours ; the precipitate which had formed was filtered off and washed with a saturated solution of ammonic sulphate. The precipitate was found to consist of strontic sulphate. On testing this in a radiant matter tube the citron band was very decided, although much fainter than in the original oxalate. The filtrate was diluted largely, heated, and precipitated with a hot solution of ammonic oxalate ; it was then allowed to stand for some time, when a bulky white calcic oxalate came down. This was filtered and washed. Tested in the radiant matter tube, after ignition and treatment with sulphuric acid, it gave the citron band, far exceeding in brightness the spectrum of the original oxalate.

9. So far all the chemical evidence went to show that the band-forming substance was calcium, and further tests tried with the purified oxalate confirmed this inference. Every analytical test to which it was subjected showed lime, and nothing but lime ; all the salts which were prepared from it resembled those of lime, both physically and chemically ; the flame spectrum gave the calcium lines with extraordinary purity and brilliancy ; and finally, the atomic weight, taken with great care, came out almost the same as that for calcium, 39·9 as against Ca 40.

10. I now sought for the citron band amongst other calcium minerals. The preliminary testing was simple. The finely powdered mineral was moistened with strong sulphuric acid, the action being assisted by heat, and the mass was then raised to dull redness (4). It was then put into a radiant matter tube and the induction spark passed through after the exhaustion had been pushed to the required degree.

Treated in this manner most native compounds of lime gave the citron band. A perfectly clear and colourless crystal of Iceland spar converted into sulphate gave it strongly, native calcic phosphate less strongly, and a crystal of arragonite much more brightly. A stalactite of calcic carbonate from the Gibraltar caves gave the band almost as well as calcite, as also did cinnamon stone (lime alumina garnet), iron slag from a blast-furnace, commercial plaster of Paris, and most specimens of ordinary burnt lime.

*The citron band not due to calcium.*

11. Evidence stronger than this in favour of the view that the citron band was an inherent characteristic of calcium could scarcely be ; but, on the other hand, there was evidence equally conclusive that the band was not essential to calcium. The ammonia precipitate (5) sometimes gave the citron band with great strength and purity, and although I had not yet obtained this in quantities sufficient for a detailed examination, it was easy to decide that it contained no phosphoric, silicic, or boric acid, fluorine, or other body likely to cause the precipitation of lime in this group. This precipitate must therefore be an earth, and the more carefully I purified it from lime and other substances, the more brilliantly shone out the citron band, and the more intense became the green and red bands.

Another stubborn fact was this :—Starting with a lime compound which showed the citron band, I could always obtain a calcic oxalate which gave the band stronger than the original substance ; but if I started with a lime compound which originally gave no citron band, I could never by any means, chemical or physical, constrain the lime or the earthy precipitate to yield a citron band.

12. Among the minerals tried was eudialyte, a silicate of zirconium, iron, calcium, and sodium, containing about 10 per cent. of lime. No citron band could be detected on testing the original mineral or any of the constituents separated from it on analysis. This, and a lump of common whiting (levigated chalk), were for some time my only sources of lime which gave no citron band.

13. The only explanation that I could see for this anomaly was that the elusive citron band was caused by some element precipitated with the calcic oxalate, but present in a quantity too small to be detected by ordinary chemical means. I then thought that were I to fractionally precipitate the solution of lime, the band-forming body might be concentrated in one or the other portion. Accordingly the calcic oxalate (7, 8, 9) was ignited and dissolved in hydrochloric acid, and fractionally precipitated in three portions with ammonic oxalate, the first and third portions being comparatively small. They were dried, ignited with sulphuric acid, and tested in the radiant matter tube. All three portions showed the citron band, but the portion which came down first gave the band decidedly the strongest, and the third portion precipitated showed it weakest. This therefore pointed to a difference between calcium and the body sought for. The process, however, was not satisfactory, and I was driven to seek some other method.

14. A portion of an ammonia precipitate found to give the citron band very well (5, 11), was dissolved in dilute sulphuric acid, and the solution evaporated down. Crystals were formed which were difficultly soluble in hot water, but appeared more soluble than calcic sulphate.

A large quantity of the calcic oxalate (7, 8, 9) was ignited with sulphuric acid at a dull red heat, and the resulting calcic sulphate was finely ground and then boiled in a

very small quantity of water—not sufficient to dissolve the one-hundredth part of it. The mass was thrown on a filter, and the small quantity of clear liquid which came through was precipitated with ammonic oxalate. The resulting white precipitate was ignited with sulphuric acid, and tested in the radiant matter tube. For the sake of comparison a portion of the calcic sulphate remaining on the filter was also put in a radiant matter tube. The sulphate from the aqueous extract gave the citron band far more brilliantly than the calcic sulphate from the filter. I found, however, that it was impossible, by any amount of washing or boiling out, to deprive the calcic sulphate of all power of giving the citron band, although it was possible in this way to weaken its intensity considerably.

## Experiments with calcic sulphate.

15. Supposing that the substance giving the citron band formed a sulphate more soluble in water than calcic sulphate, it was anticipated that repeated washings with cold water would extract some of it, which might then be detected more easily. About four pounds' weight of commercial plaster of Paris, which showed very faint traces of the citron band, were mixed with water and rapidly poured on a large filter. Before the mass solidified a slight saucer-like depression was made in the upper part, and a few ounces of water were poured on. This ran through slowly, and it was then poured back and the exhaustion repeated several times. The aqueous extract was then evaporated to dryness, ignited with sulphuric acid, ground in a mortar with small successive quantities of water, the liquid boiled, filtered, and precipitated, first with ammonia, and the filtrate with ammonic oxalate. These precipitates both showed the citron band very fairly, far more intensely than it was seen in the original calcic sulphate. The green and red bands were also visible.

The same mass of plaster of Paris was then washed, as before, with a little dilute hydrochloric acid passed through several times, and this extract was treated in the same way by evaporation and extraction with water, and the filtrate precipitated, first with ammonia, and then with ammonic oxalate. In these precipitates the citron band, together with the green and red bands, were much more brightly manifest than in the precipitates from the aqueous extract.

## Wide distribution of the citron band-forming body.

16. These experiments are conclusive in proving that the citron band is not due to calcium, but to some other element, probably one of the earthy metals, occurring in very minute quantities, but widely distributed along with calcium, and I at once commenced experiments to find a more abundant supply of the body sought for. Amongst other substances tested I may note the following as giving a more or less decided citron band in the spectrum when treated with sulphuric acid in the manner indicated above (10) :—Crystallised barytic chlorate, heavy spar, common limestone, strontic nitrate, native strontic carbonate, crystallised uranic nitrate, commercial

magnesic sulphate, commercial potassic sulphate, Wagnerite (magnesic phosphate and fluoride), zircon, cerite, and commercial ceric oxalate.

## *Examination of zircon for the citron band.*

17. Some specimens of zircon treated in the above manner appeared sufficiently rich to make it probable that here might be found an available source of the citron-band-yielding body. I found it in crystals from Green River, North Carolina, from Ceylon, from Expailly, from Miask (Oural), and from Brevig, and having a good supply of North Carolina zircons I started working up these in the following manner :—

The finely-powdered zircons were fused with sodic fluoride, and the melted mass powdered, boiled with sulphuric acid, and filtered. The solution was precipitated with excess of ammonia, the precipitate well washed and dissolved in hydrochloric acid, and the solution made nearly neutral. A little zirconic oxychloride sometimes separated on evaporation; this was filtered off. An excess of sodic thiosulphate was now added, and the whole boiled for some time until a portion of the filtrate gave no further precipitate on boiling again with sodic thiosulphate. The precipitated zirconic thiosulphate was worked up for zirconia; it was found to be quite free from the substance giving the citron band. The solution filtered from the zirconic thiosulphate was precipitated with ammonia, and the brown gelatinous precipitate was well washed. The filtrate was precipitated with ammonic oxalate, which brought down much calcic oxalate. This showed the citron band, but not strongly. The brown gelatinous precipitate was dissolved in nitric acid. Argentic nitrate was added to separate chlorine, and the filtrate from the argentic chloride was boiled down with nitric acid and excess of metallic tin to separate phosphoric acid. The clear solution, separated from the stannic oxide, phosphate, &c., was boiled down with hydrochloric acid to remove nitric acid, and then saturated with hydric sulphide to separate silver and tin.

18. The filtrate from the sulphides was freed from hydric sulphide by boiling, and was then mixed with tartaric acid and excess of ammonia, to precipitate any yttria that might be present, together with FORBES's zirconia $\beta$ * (jargonia?). On standing for some hours this gave a small quantity of a precipitate, which was separated by filtration; it was tested in the radiant matter tube, and found not to give the citron-band spectrum (44). To the filtrate ammonic sulphide was added to precipitate the iron. The black precipitate was filtered off, and the filtrate evaporated to dryness, and ignited to destroy the organic matter. The residue, heated with sulphuric acid and ignited, gave the citron spectrum very brightly. This would probably be the earth which FORBES calls zirconia $\gamma$.†

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* 'Chem. News,' vol. 19, p. 277.

† *Loc. cit.*

19. For many years chemists have suspected that what is known as zirconia might be a compound. SVANBERG* found that zircons from different localities varied in specific gravity, and the earth or earths obtained by fractional precipitation with oxalic acid had not the same properties, the hydrogen equivalents of the metals of the earths of the different fractions varying from 17·01 to 27·3, the metal of the earth hitherto recognised as zirconia being 22·4.† He considered zirconia to contain two different earths, the oxalate of one being less soluble in acid than that of the other, and their sulphates differing in crystalline form and solubility. He proposed the name "noria" for one of the earths, retaining that of zirconia for the other. The researches of BERLIN, on the other hand, seem to disprove this.

20. Remembering the remarkable result produced in the absorption spectrum of some jargons by the presence of a minute trace of uranium,‡ I tried numerous experiments with this metal, adding small quantities of it to zirconia, lime, thoria, ceria, &c., but in no case could I educe the citron-band spectrum by this means.

I may condense a year's work on zircon,—more than ten pounds weight of crystals from North Carolina having been worked up—by stating that the result was comprised in about 300 grains of an earthy residue (18), and about two ounces of oxalate, chiefly calcium; the former gave the citron band very well. The process as detailed above is given, since by this means a very large quantity of zircons was worked up, affording me the material which ultimately enabled me to solve the problem which at one time seemed almost hopeless.

The zirconia prepared from these zircons when tested sometimes showed the citron band, especially after precipitation as an oxychloride. Zirconia precipitated as thiosulphate did not yield the citron band (28). A zirconia rich in citron band, fractionally precipitated by ammonia, yielded precipitates of increasing richness, the last fraction showing the citron band strongly.

21. The calcic oxalate obtained from zircon gave unsatisfactory results, so attention was directed to the earthy residue (18). This was found to be of highly complex character, containing thoria (which had escaped precipitation as thiosulphate), ceria, lanthana, didymia, yttria, and probably some of the newly-discovered rarer earths.

### Examination of cerite for the citron band.

22. The position of the citron band in the spectrum falls exactly on the strongest absorption band of didymium, so that a piece of didymium glass or cell of solution of the nitrate entirely obliterates the citron band. This naturally suggested that the band was due to didymium.

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* POG. Ann., vol. 65, p. 317.

† SVANBERG's numbers for these earths are 938 to 1320 ($M_2O_3$), the earth hitherto recognised as zirconia being 1140; oxygen being 100. For the sake of uniformity I have recalculated his equivalents for the metals on the $O = 16$ scale, taking the formula as $M_2O$ (see note 1, par. 40).

‡ 'Chem. News,' vol. 19, pp. 121, 142, 205, 277; vol. 20, pp. 7, 104; vol. 21, p. 73.

Cerite was accordingly the next mineral experimented on. The powdered mineral tested in the tube in the original way gave a good citron band. It was made into a paste with sulphuric acid, and after all action had ceased it was extracted with cold water. The earths were then precipitated with ammonic oxalate, and the oxalate ignited. The fawn-coloured powder was then converted into sulphate, dissolved in water, and the cerium metals precipitated by long digestion with excess of potassic sulphate. When no didymium bands could be detected in a considerable thickness of the supernatant liquor it was assumed that all the cerium metals were down, and the liquid was filtered.

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.

24. This experiment proved the inadequacy of the didymium explanation (22), and further tests showed that not only could I get no citron band in pure didymium compounds, but the spectrum entirely failed to detect didymium in many solutions of the earth which gave the citron band brilliantly.

25. Attention was now turned to the solution filtered from the insoluble double sulphates from cerite (22). Potash in excess was added to the filtrate, and the flocculent precipitate filtered off, and after well washing was converted into sulphate, and tested in a radiant matter tube. The spectrum, of extraordinary brilliancy, was far brighter than any I had hitherto obtained. Unfortunately, however, the quantity was too small to be subjected to very searching chemical analysis.

### Examination of thorite and orangite.

26. Search was next made amongst other minerals rich in the rarer earths. Thorite, another disputed mineral, was finely powdered, treated with sulphuric acid, and tested in the radiant matter tube. It gave the citron spectrum most brilliantly —equal, in fact, to the mixture of earths obtained from zircons (18, 21) at so great an expenditure of time and trouble. Orangite treated in the same manner gave almost as good a spectrum. Pure thorinic sulphate prepared by myself was found not to give the citron band, but three specimens prepared and given to me by friends all gave it, so it was not unlikely that in thorite and orangite might at last be found a good source of the long-sought element—that in fact the body I was hunting for, if not thorina, might possibly be BAHR's hypothetical wasium. Having obtained about 2 lbs. of orangite and thorite, they were worked up as follows :—

27. The finely-powdered mineral was heated for some time with strong hydrochloric acid, and when fully gelatinised and all action had ceased, it was evaporated to dryness to render the silica insoluble ; then extracted with water slightly acidulated with hydrochloric acid, boiled, and filtered. Hydric sulphide was passed through the

filtrate for some time. The flask then corked was set aside for twenty-four hours and filtered. The filtrate was evaporated to a small bulk, nearly neutralised with ammonia, and then boiled for some time with excess of sodic thiosulphate. This precipitated the thorina, alumina, zirconia, and titanic acid, whilst it left in solution the metals of the cerium and yttrium groups. The filtrate was boiled down to a small bulk, when a further precipitation took place : this was filtered off and added to the first thiosulphate precipitate. To the clear filtrate excess of ammonic oxalate was added, and the whole allowed to rest twenty-four hours. The precipitated oxalates were filtered, washed, ignited, dissolved in hydrochloric acid, and the excess of acid evaporated off. The aqueous solution was then mixed with a large excess of freshly precipitated baric carbonate, and set aside for twenty-four hours with frequent shaking (29). This would precipitate much of the cerium, and any iron or alumina which might have escaped previous treatment. The liquid was filtered from the precipitate produced by baric carbonate, and the clear solution, which would contain nothing but barium, and some of the yttrium and cerium metals, was treated as described further on (30).

28. The thiosulphate precipitate tested in the radiant matter tube gave no citron band, nor did it seem possible to detect this band on testing the purified thorina obtained from this precipitate, nor from the alumina or zirconia from the same precipitate. This confirmed the results obtained when working up zircons, that sodic thiosulphate did not precipitate the citron band-forming body.

29. The barium precipitate (27) was dissolved in hydrochloric acid, the baryta separated with sulphuric acid, and the solution precipitated with ammonic oxalate. The ignited precipitate, which amounted to 0·223 per cent. of the mineral taken, contained the cerium metals. On testing in a radiant matter tube it gave the citron band only moderately well—not nearly so strong as the original thorite and orangite. The iron and alumina in the filtrate from the ceric oxalates were likewise precipitated and tested ; they showed a faint trace of citron band.

30. The solution (27) filtered from the barium precipitate was freed from baryta by sulphuric acid, precipitated with ammonic oxalate, and the precipitate washed and ignited ; it amounted to only 0·125 of the mineral taken. Tested in the radiant matter tube it showed the citron band about as well as the corresponding earth from the barium precipitate.

This was disheartening, for after having started with a mineral which gave the citron band well, and having hunted the citron band as it were into a corner, the only result was two trifling precipitates showing the citron band less intensely than did the raw material itself. The experiment, however, proved one thing : the band-forming substance was not thorina. The occurrence of this spectrum must therefore be due to some other element present in small quantity in thorite and orangite.

31. The two mixtures of earths—the one from the barium precipitate (29) and the other from the barium filtrate (30)—which showed the citron line moderately well,

were dissolved in sulphuric acid, the solution neutralised as nearly as possible with potash, and digested for several days with excess of potassic sulphate. The solution, which at first showed the didymium bands, was then found to be free from didymium.

32. The insoluble double sulphates were filtered and washed with a cold saturated solution of potassic sulphate. The precipitate was boiled for some time in ammonia, filtered, dissolved in hydrochloric acid, and precipitated with ammonic oxalate. This precipitate was ignited and tested in the radiant matter tube. It gave scarcely a trace of citron band (23). The earth was further purified by the potash and chlorine method, and was found to consist principally of ceric oxide.

33. The solution filtered from the insoluble potassio-ceric sulphate (31) was boiled with ammonia and ammonic sulphide. A small quantity of a white flocculent earth came down—too small a quantity to weigh. Tested in a radiant matter tube, it gave the citron band better than either of the above precipitates, showing that by this treatment the body had been concentrated (25).

34. It seemed possible that the earth sought for might be present in larger quantity in the thorite, but that it had been gradually carried down mechanically or by mass-action rather than chemically, by the numerous operations it had undergone before getting it to the final stage. Therefore a fresh quantity of thorite was extracted with hydrochloric acid. The solution was precipitated with potassic sulphate, taking the usual precautions to secure complete precipitation. A bulky precipitate ensued, which contained the thorina and cerium earths. These were separated and tested, and found to give only a faint citron band.

35. The solution of earthy sulphates soluble in potassic sulphate was precipitated with ammonic oxalate. The precipitate ignited with sulphuric acid, and tested in a radiant matter tube, gave the citron spectrum with great brilliancy (25, 33).

*Chemical facts connected with the citron body.*

36. Certain chemical facts concerning the behaviour of the sought-for element which came out during the course of the tentative trials already described had considerably narrowed the list amongst which it might probably be found. All the evidence tended to show that it belongs to the group of earthy metals, consisting of aluminium, beryllium, thorium, zirconium, cerium, lanthanum, didymium, and the yttrium family, together with titanium, tantalum, and niobium. The sought-for earth is insoluble in excess of potash (25); this excludes aluminium and beryllium. It is not precipitated by continued boiling with sodic thiosulphate (17, 27); this excludes aluminium, thorium, and zirconium. Fused with acid potassic sulphate, the resulting compound is readily soluble in cold water; this excludes tantalum and niobium. Evaporating to dryness with hydrochloric acid and heating for some time does not render the mass insoluble in water (27); this excludes titanium and silicium. It is easily soluble in an excess of a saturated solution of potassic sulphate (25, 33, 34); this excludes thorium, the cerium group, some of the numerous members of the

yttrium group, and zirconium. The only remaining elements among which this elusive body would probably be found are those members of the yttrium family which are not precipitated by potassic sulphate.

37. On the other hand, the body giving the citron band spectrum did not behave like one of the known earths. A rich residue was fused with sodic carbonate, and the mass extracted with water. The insoluble residue, on testing in the usual way, was rich in citron band, but subsequent treatment of the aqueous solution gave me an earth which also gave the citron band strongly.

An acid solution of the citron body was precipitated by ammonia and ammonic chloride. The earth was not completely precipitated, but after a long boiling some remained in solution. I have since ascertained that the detection of the citron-band body in solution under these circumstances is only owing to the marvellous delicacy of the test, which carries our powers of recognition far beyond the resources of ordinary chemistry.

38. Besides obtaining indirect evidence that the citron band was not due to certain elements, I tried special experiments with each substance, brought to the highest possible state of purity. In many cases I detected more or less traces of citron band ; but I had come to the conclusion, abundantly warranted by facts, that this citron band was an extraordinarily sensitive test of the presence of the element causing it ; and the minute chemistry of many of these earthy metals being insufficiently known, it was not surprising that traces of one of them should adhere to another in spite of repeated attempts to purify it out. With each successive fractional precipitation the citron band became fainter, showing that with perseverance the last trace would probably disappear. The time this process would have occupied, in my opinion, seemed not worth the little additional evidence it would have afforded.

39. Taking into consideration the extremely small quantity of phosphorescent material which had so far been obtained, all these experiments justified me in assuming that the body sought for not only belonged to the group of earths, but also most probably to the sub-group not precipitated by potassic sulphate to which yttria belongs. As, however, the number of these metals has increased so much within the last few years, and as the quantity of material which I had up to the present at my disposal was too small to admit of a satisfactory chemical examination being made of it, search was commenced among other sources known to be rich in these metals. Besides, not only did the majority of the substances I had up till now obtained in anything like quantity indicate the citron band earth to belong to the yttria group (33, 34, 36), but also that either the earth itself showed an absorption band in the spectroscope, or was invariably accompanied by one which did. On the other hand, I had a certain amount of evidence that the earth sought for did not show a band in the spectroscope (24) ; but remembering the extremely small quantity of very impure substance experimented with, the evidence on this point was not at all conclusive.

### The sought-for body one of the yttrium family.

40. The yttria earths form a somewhat numerous family. Fortunately for chemists, a mineral rich in yttria earths—samarskite—has been found in large quantity in Mitchell County, North Carolina, and to this mineral I accordingly now directed my attention.

The following list of elements of the yttrium and its allied families, said to occur in samarskite and similar minerals, may be considered complete to the present time.

| Name. | Absorption Spectrum. | Hydrogen equivalent of Metal.[1] (Type of Oxide $M_2O$.) |
|---|---|---|
| Cerium . . . . . . . . . | No | 47·1 [2] |
| Columbium[3] . . . . . . . . | Yes | — |
| Decipium . . . . . . . . . | Yes | 57·0 [4] |
| Didymium . . . . . . . . . | Yes | 48·5 [5] |
| Didymium $\beta$ . . . . . . . . | Yes | 47·0 [6] |
| Erbium . . . . . . . . . | Yes | 55·3 [7] |
| Holmium[8] . . . . . . . . | Yes | 54·0 [9] |
| Lanthanum . . . . . . . . . | No | 46·0 [10] |

[1] As it is at present doubtful whether the oxides of several of the metals in this table belong to the type $M_2O$, $M_2O_3$, or $MO$, I have, for the sake of uniformity and simplicity, in calculating the values from the composition of their salts, by which these metals are chiefly discriminated, taken the type of oxide to be $M_2O$.

[2] BÜHRIG, 'J. Pr. Chem.,' ser. 2, vol. xii., p. 209.

[3] Dr. J. LAWRENCE SMITH in a paper read before the United States National Academy of Sciences in 1879, announced the discovery in Samarskite of two new elements, which he named Columbium and Rogerium ('Nature,' vol. xxi., p. 146). I have failed to find any further notice of these elements. This Columbium must not be confounded with the well-known Columbium, sometimes called Tantalum.

[4] DELAFONTAINE, 'Comptes Rendus,' vol. lxxxvii., p. 632, vol. xciii., p. 63; 'Chemical News,' vol. xxxviii., p. 223, vol. xliv, p. 67.

[5] CLÈVE, 'Bull. Soc. Chim.,' ser. 2, vol. xxi., p. 246; BRAUNER, 'Comptes Rendus,' vol. xciv., p. 1718; 'Chemical News,' vol. xlvii., p. 175.

[6] CLÈVE, 'Comptes Rendus,' vol. xciv., p. 1528; 'Chemical News,' vol. xlv., p. 273. BRAUNER, 'Comptes Rendus,' vol. xciv., p. 1718; 'Chemical News,' vol. xlvi., p. 16.

[7] CLÈVE, 'Comptes Rendus,' vol. xci., p. 381; 'Chemical News,' vol. xlii., p. 199. LECOQ DE BOISBAUDRAN, 'Comptes Rendus,' vol. lxxxix., p. 516; 'Chemical News,' vol. xl., p. 147.

[8] Called by SORET, the first discoverer, "X." Subsequently CLÈVE discovered the same metal and called it holmium. SORET has now adopted CLÈVE's name. 'Comptes Rendus,' vol. lxxxix., p. 708, and vol. xci., p. 378; 'Chemical News,' vol. xl., p. 224, and vol. xlii., p. 199. LECOQ DE BOISBAUDRAN, 'Comptes Rendus,' vol. lxxxix., p. 516; 'Chemical News,' vol. xl., p. 147.

[9] CLÈVE, 'Comptes Rendus,' vol. lxxxix., p. 478; 'Chemical News,' vol. xl., p. 125.

[10] BRAUNER, 'Comptes Rendus,' vol. xciv., p. 1718; 'Chemical News,' vol. xlvi., p. 16.

| Name. | Absorption Spectrum. | Hydrogen equivalent of Metal. (Type of Oxide $M_2O$). |
|---|---|---|
| Mosandrum . . . . . . . . . | No | $51 \cdot 2$ [11] |
| Philippium ([12]) . . . . . . . | No | — |
| Rogerium([13]) . . . . . . . . | Yes | — |
| Samarium . . . . . . . . . . | Yes | $50 \cdot 0$ [14] |
| Scandium . . . . . . . . . . | No | $14 \cdot 7$ [15] |
| Terbium . . . . . . . . . . | No | $49 \cdot 5$ [16] |
| Thorium . . . . . . . . . . | No | $58 \cdot 4$ |
| Thulium . . . . . . . . . . | Yes | $56 \cdot 5$ [17] |
| Ytterbium . . . . . . . . . | No | $57 \cdot 9$ [18] |
| Yttrium . . . . . . . . . . | No | $29 \cdot 7$ [19] |
| Yttrium $\alpha$ . . . . . . . . . | No | $52 \cdot 2$ [20] |
| Yttrium $\beta$ . . . . . . . . . | Yes | $49 \cdot 7$ [21] |
| Zirconium . . . . . . . . . | No | $22 \cdot 5$ |

[11] LAWRENCE SMITH, 'Comptes Rendus,' vol. lxxxvii., pp. 145, 146, 148. MARIGNAC, *ibid.*, vol. lxxxvii., p. 281. DELAFONTAINE, in October, 1878 (*ibid.*, vol. lxxxvii., p. 600), considers mosandrum a mixture of terbium, yttrium, erbium, didymium, and philippium. Subsequently, however, LAWRENCE SMITH, in November, 1878 (*ibid.*, vol. lxxxvii., p. 831), adduces chemical and other reasons to show that his mosandrum is not a mixture, but a true element. A year later, September 1, 1879 (*ibid.*, vol. lxxxix., p. 480), LAWRENCE SMITH repeats the claim for mosandrum to be classed with the elements.

[12] DELAFONTAINE, 'Comptes Rendus,' vol. 87, p. 559; Chemical News,' vol. 38, p. 202; 'Jour. Chem. Soc.,' vol. 36, p. 116.

[13] *See* Note ([3]) to Columbium, *ante.*

[14] LECOQ DE BOISBAUDRAN, 'Comptes Rendus,' vol. lxxxviii., p. 322, and vol. lxxxix., p. 212; 'Chemical News,' vol. xxxix., p. 115, and vol. xl., p. 99. BRAUNER, 'Chemical News,' vol. xlvii., p. 175; CLÈVE, 'Comptes Rendus,' vol. xcvii., p. 94; 'Chemical News,' vol. xlviii, p. 39.

[15] NILSON, 'Comptes Rendus,' vol. xci., p. 118; 'Chemical News,' vol. xlii., p. 83. CLÈVE, 'Comptes Rendus,' vol. lxxxix., p. 419; 'Chemical News,' vol. xl., p. 159.

[16] MARIGNAC, 'Ann. Chim. et Phys.,' ser. 5, vol. xiv., p. 247; 'Journ. Chem. Soc.,' vol. xxxvi., p. 113. DELAFONTAINE, 'Ann. Chim. et Phys.,' ser. 5, vol. xiv., p. 238; 'Journ. Chem. Soc.,' vol. xxxvi., p. 114.

[17] CLÈVE, 'Comptes Rendus,' vol. lxxxix., p. 478, and vol. xci., p. 328; 'Chemical News,' vol. xl., p. 125, and vol. xlii., p. 182. THALÈN, 'Comptes Rendus,' vol. xci., p. 376; 'Chemical News,' vol. xlii., p. 197.

[18] MARIGNAC, 'Comptes Rendus,' vol. lxxxvii., p. 578; 'Chemical News,' vol. xxxviii., p. 213. NILSON, 'Comptes Rendus,' vol. lxxxviii., p. 642, vol. xci., p. 56; 'Chemical News,' vol. xlii., p. 61.

[19] CLÈVE, 'Comptes Rendus,' vol. xcv., p. 1225; 'Chemical News,' vol. xlvii., p. 4. 'Bull. Soc. Chim.,' vol. xxxix., p. 120; 'Chemical News,' vol. xlvii., p. 143.

[20] MARIGNAC, 'Comptes Rendus,' vol. xc., p. 899; 'Chemical News,' vol. xli., p. 250.

[21] This is almost certainly identical with LECOQ DE BOISBAUDRAN's samarium. See MARIGNAC, 'Comptes Rendus,' vol. xc., p. 899; 'Chemical News,' vol. xli., p. 250. SORET, 'Comptes Rendus,' vol. xci., p. 378; 'Chemical News,' vol. xlii., p. 199.

41. Some of these claimants will certainly not stand the test of further scrutiny. Thus samarium and yttrium $\beta$ are in all probability identical; and I should scarcely have included philippium, as ROSCOE* has conclusively proved that this is a mixture of terbium and yttrium, and my own results (61) confirm those of ROSCOE. Moreover, others of these so-called elements will probably turn out to be mixtures of known elements. But in the confessedly very imperfect state of our knowledge of the chemistry of these metals it is not safe for me in this research to assume that any one of them will surely not survive. The complete list as it stands will therefore be taken to contain all hitherto claimed as new, although it is almost certain to include too many.

*The sought-for body has no absorption spectrum.*

42. In the second column " Yes " or " No " indicates whether the solutions give an absorption spectrum when examined by transmitted light. Now could I definitely settle whether solutions of the citron-band body gave an absorption spectrum or not, I could at once eliminate a whole class of elements.

This was not difficult to determine. I have already said (22, 24) that spectroscopic examination entirely failed to detect didymium in many solutions of the earth which gave the citron band strongly. This was not always the case. In early days of this research I frequently obtained absorption bands innumerable when the citron-band body was known to be present; but as I became better acquainted with the chemical reactions of the new earth I gradually succeeded in eliminating one after the other those metals yielding absorption spectra. The earth from zircons (18, 21) gave the most satisfactory results in this respect. This, after removing the little didymium present, gave but a trace of an absorption spectrum, which from its general appearance was probably due to erbia. The earth obtained from cerite (25), which gave the citron spectrum with great brilliancy, on the other hand yielded no absorption spectrum; and generally I may say that, whenever I started with a sufficient quantity of an earth giving both citron-band spectrum and absorption spectrum, I could, by appropriate chemical means, always separate it into three portions,— one which gave the citron-band spectrum with great brilliancy, and showed in concentrated solution a very faint absorption spectrum, and frequently none at all; another which gave very little citron-band spectrum, but a good absorption spectrum; and a third intermediate portion— about four-fifths of the whole—which gave both citron band and absorption spectrum. This portion, by repetition of the treatment, could again be split up in the same way, and the operation repeated as often as the stock of material held out.

43. Having definitely settled the question that the metal giving the citron-band spectrum was not one of those giving an absorption spectrum, the possible elements become materially narrowed to the following list :—Cerium, lanthanum, mosandrum, scandium, terbium, thorium, ytterbium, yttrium, yttrium $\alpha$, and zirconium.

* 'Jour. Chem. Soc.,' vol. 41, p. 277.

Of these the potassic sulphate reaction (36) excludes cerium, lanthanum, scandium, thorium, yttrium α, and zirconium, so there are left only the following :—

<div align="center">

Mosandrum,

Terbium,

Ytterbium,

Yttrium.

</div>

44. Certain chemical reactions for a long time made me dismiss yttrium from the list of likely bodies. In my analysis of zircons (18), towards the latter part of the process, I used the following process to separate the iron :—The solution, mixed with tartaric acid and excess of ammonia, was allowed to stand for some time. A small quantity of a precipitate gradually formed, which was filtered off, and it was this filtrate, after separating the iron with ammonic sulphide, that yielded the greatest quantity of substance giving the citron band. Now one of the methods of separating yttria from alumina, berylla, thoria, and zirconia is to precipitate it as tartrate in the presence of excess of ammonia, the other earths remaining in solution. FRESENIUS says : —"The precipitation ensues only after some time, but it is complete."

The precipitate thus obtained with tartaric acid and ammonia should therefore contain all the yttria : *it gave no citron band whatever in the radiant matter tube ;* whilst the residue, which should be free from yttria (18), proved for a long time the only source of material wherewith to investigate the chemical properties of the body giving the citron spectrum.

45. Another reason which made me, at this stage of the research, pass over yttria, was that I had already tested this earth in the radiant matter tube. In a paper on "Discontinuous Phosphorescent Spectra in High Vacua," read before the Royal Society, May 19th, 1881,[*] I said—"Yttria shows a dull greenish light giving a continuous spectrum " (75).

For these reasons I for a long time omitted yttria from my list of possible bodies, and considered that the earth, if not a new one, might turn out to be either mosandra, terbia, or ytterbia.

<div align="center">

*Analysis of samarskite.*

</div>

46. A very large quantity (about 15lbs. weight altogether) of samarskite was worked up, partly by the hydrofluoric acid method of LAWRENCE SMITH,[†] and partly by fusion with potassic bisulphate. The niobic and tantalic acids after purification were found to give no citron band spectrum.

These methods both gave as a result a large quantity of mixed earths containing most, if not all, of the bodies enumerated in par. 40. Tested in the radiant matter tube, this material gave the citron spectrum very brilliantly. It was dissolved in hydrochloric acid, neutralised as nearly as possible with ammonia, and boiled with

<div align="center">

[*] Proc. Roy. Soc., No. 213, 1881.

[†] 'Comptes Rendus,' vol. 87, p. 146.

</div>

sodic thiosulphate. This precipitated the thoria, zirconia, and alumina. In this precipitate some of the scandia might also be found, if present in quantity, but as scandic thiosulphate is not completely precipitated, and the earth is present only in minute traces, not much scandia, it is probable, was thus carried down.

This thiosulphate precipitate, treated in the usual way with sulphuric acid, gave no citron band in the radiant matter tube.

47. The filtrate from the thiosulphate was precipitated hot with excess of ammonia, and the precipitate after washing treated with sulphuric acid, dried, and heated till fumes of sulphuric acid disappeared. The sulphate, whitish with a very pale rose tint, was finely ground, and dissolved with frequent agitation in the smallest possible quantity of cold water—an operation which required much time. The solution was then precipitated with potassic sulphate, taking all necessary precautions to keep the liquid well saturated with potassic sulphate. This operation was allowed to go on for about ten days, when the precipitated double sulphates were filtered off and slightly washed with a saturated solution of potassic sulphate. The precipitate contained cerium, lanthanum, didymium, didymium β, decipium, samarium, scandium, yttrium α, yttrium β, together with any thorium and zirconium which might have escaped the thiosulphate treatment.

48. The filtrate from the double sulphates was precipitated hot with ammonia, which brought down the erbia, holmia, mosandra, terbia, thulia, ytterbia, and yttria. The small quantity of manganese in solution was in this operation completely thrown out.

49. The insoluble double sulphates (45) were dissolved in hydrochloric acid, precipitated hot with ammonia, washed till free from potassium salts, re-dissolved, precipitated as oxalates, ignited, and set aside for further examination. On testing in the radiant matter tube this mixture of oxides was found to be practically free from citron band.

50. The ammonia precipitate from the sulphates soluble in potassic sulphate (46) was well washed till free from potassium salts, and dissolved in excess of nitric acid. The concentrated solution gave an absorption spectrum showing lines belonging to erbium and allied metals. Having already proved that the body I was seeking was not one of those metals which gave an absorption spectrum (42, 43), my first object was to find some method by which I could roughly separate this mixture of earths into two portions, one giving absorption bands, and the other having no action on the transmitted spectrum. I found this was possible by taking advantage of the different solubility of the oxalates in nitric acid.

51. The highly acid solution of the nitrates was fractionally precipitated in the following manner :—

To the boiling liquid a solution of ammonic oxalate was added drop by drop. The precipitate at first formed re-dissolved on stirring. The cautious addition of ammonic oxalate was repeated until the precipitate refused to dissolve entirely, but left the hot liquid somewhat milky. It was then rapidly cooled with constant stirring, which

brought down a heavy crystalline oxalate. This was filtered off, and called oxalate A. The filtrate, again heated to boiling, was precipitated in exactly the same way with a further quantity of ammonic oxalate till the hot liquid became opalescent. On cooling and stirring, a farther quantity of oxalate came down. The filtrations and precipitations were repeated until no more precipitate could be obtained. Usually I could get twelve or thirteen fractionations in this manner; towards the end the solution did not get milky, and it had to stand sometimes twenty-four hours before much oxalate came down.

52. The fractions first precipitated by oxalic acid gave very strong absorption bands when the concentrated solutions of the oxides were examined by transmitted light. The fractions last precipitated showed the absorption bands only faintly.

53. These operations gave me oxalates from A to L. These, ignited, with free access of air, were then each dissolved in nitric acid, and again separately fractionated as oxalates. The result was about 150 precipitates, ranging from $A_1 A_2 \ldots A_{12}$, $B_1 B_2 \ldots B_{12}$, to $L_1 L_2 \ldots L_{12}$.

These, after ignition, were separated into five lots according to order of colour, and the fractionation of each of the five lots repeated as already described; the series of operations now closely resembling those of PATTINSON's process for desilvering lead. This gave me about sixty lots. This time the hydrogen equivalent of the metal of each lot was taken by converting the oxalate into sulphate and estimating the sulphuric acid, assuming $M_2O$ to be the type of oxide (40, note 1). The result was a series of earths having hydrogen equivalents (M) ranging from about 48 to 33. The earths were now sorted into high, low, and intermediate, those giving intermediate H equivalents being re-fractionated with repeated H equivalent estimation, the highest and lowest being each time separated and added to the former high and low lots.

54. The ultimate result of about five hundred fractional precipitations gave me a mixture of earths having an H equivalent M = 48, and showing a strong absorption spectrum (56); a mixture having an H equivalent M = 33, having no absorption spectrum (65); and intermediate earths.

In the radiant matter tube all these fractions gave the citron-band spectrum well, but that of the earth of lowest equivalent was much the brightest, and that of the highest equivalent the least intense.

55. Three methods are available for the partial separation of these earths and for the complete purification of any one of them. The formic acid process (56, 57) is best for separating terbia, as terbic formate is difficultly soluble in water, the other formates being easily soluble.

Fractional precipitation with oxalic acid (63, 64, 65) separates first erbia, holmia, and thulia, then terbia, and lastly yttria. This is the only method which is applicable for the separation of small quantities of terbia from yttria.

Fusing the nitrates (60, 68, 69) separates ytterbia, erbia, holmia, and thulia from yttria. It is not so applicable when terbia is present, and is most useful in purifying

the gadolinite earths. This process is the only one known for separating ytterbia from yttria.

Selection must be made of these methods according to the mixture of earths under treatment, changing the method as one earth or the other becomes concentrated on one side or thrown out on the other. Each operation must be repeated many times before even approximate purity is attained. The operations are more analogous to the separation of members of homologous series of hydrocarbons by fractional distillation than to the separations in mineral chemistry as ordinarily adopted in the laboratory.

### Preparations of pure terbia.

56. The mixture of high equivalent earths (54) richest in terbia, erbia, holmia, and thulia was treated as follows :—

The earths were dissolved in dilute formic acid, and the solution heated for some time. A white powder of terbic formate separated. This was filtered off, the solution containing the more easily soluble formates evaporated to dryness, and ignited. In this way the $M = 48$ earths were separated into two lots, one rich in terbia and the other rich in erbia, &c. The treatment with formic acid was again repeated on both lots, and the crude terbia finally purified as follows :—

57. The crude terbia from all the operations was systematically treated by the formic acid process, keeping the liquid so dilute that only a portion of the terbic formate separated out each time. The syrupy solution of formates was treated as described further on (60). The hydrogen equivalent of the terbium was taken each time; latterly it kept pretty constant at 49·5. The terbia was also tested in the radiant matter tube. At first the citron spectrum was very strong; gradually, however, it got fainter and fainter under the repeated formic treatment, until finally the spectrum became so weak as to satisfy me that it was due only to impurity in the terbia, and that, had the material been sufficient to stand against the extravagant process of purification adopted, I should finally have got a terbia giving no citron-band spectrum. (Subsequent examination (87) showed me that this terbia did not contain more than 1-5000th part of yttria.)

58. A concentrated solution of the purest terbia obtained in this way, when examined by the spectroscope, showed no absorption lines whatever: proving the absence of erbium, holmium, and thulium.

59. The hydrogen equivalent (49·5) would not definitely show the absence of ytterbium (57·9) and yttrium (29·7); but these would have been separated by the formic acid treatment, terbic formate requiring 30 parts of water for its solution, whilst yttric and ytterbic formates dissolve in less than their own weight of water. Moreover, it was not probable that the terbia contained an appreciable quantity of any of these earths as an impurity, for neither the oxalic acid, the fusing nitrate, nor the formic acid process of fractionation produced any change in the atomic weight, 49·5.

*Preparation of mixed erbia, holmia, and thulia free from other earths.*

60. The filtrate from the terbic formate (57), rich in erbia, and containing besides terbia, holmia, thulia, and yttria, was now treated by converting it into nitrates, evaporating to dryness, and submittting the mass to careful fusion, stopping the operation when the liquid mass began to evolve nitrous fumes. The erbic, holmic, and thulic nitrates decomposing before the yttric nitrate, extraction with water gave an insoluble residue rich in erbia, holmia, and thulia, and a filtrate rich in yttria. The insoluble residue was dissolved in nitric acid, again evaporated to dryness, and fused. These operations were repeated eight or ten times, with the result of raising the H equivalent of the erbium metals to about 56·8, but the citron-band spectrum remained strong for some time after. It, however, ultimately disappeared. A concentrated solution of this erbic, &c., nitrate showed a beautiful and intense absorption spectrum. I did not attempt any separation of erbium, holmium, and thulium from each other, as the evidence here obtained is sufficient to show that the element giving the citron-band spectrum is not one of these three metals. Likewise I had far too little material to enable me to enter on a work of such difficulty with any prospect of success.

## Philippia.

61. The so-called philippia was sought for in the portion of earths intermediate between the terbia and yttria (54). These were dissolved in dilute formic acid, and the solution, filtered from some terbic formate which would not dissolve, was carefully evaporated down to a small bulk, filtering off the terbic or other difficultly soluble formates as they deposited. The clear concentrated solution was then set aside over sulphuric acid to crystallise. In the course of a few days brilliant rhombic prisms crystallised out, having exactly the appearance described by DELAFONTAINE.* The finest of these crystals were picked out, dried on blotting-paper, and analysed. The hydrogen equivalent was found to be $M = 38·2$. The citron-band spectrum in the radiant matter tube was very brilliant. The solution decanted from these crystals was evaporated to a syrupy consistency, filtered from insoluble terbic formate which deposited, and treated for yttria (65).

Some of the best rhombic crystals were added to cold water acidulated with formic acid, and gently heated, but all attempts to dissolve and re-crystallise them failed. A large quantity of an insoluble formate separated, and the mother-liquor on concentration again deposited shining rhomboidal crystals. On attempting to re-crystallise these, they again deposited an insoluble white powder. The mother-liquor was found to contain a large quantity of yttria, and the white insoluble formate on ignition gave an earth having the atomic weight and chemical behaviour of terbia. This entirely

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* 'Comptes Rendus,' vol. 87, p. 559; 'Chemical News,' vol. 38, p. 202; 'Journ. Chem. Soc.,' vol. 36, p. 116.

corroborates Professor Roscoe's conclusions,* that Delafontaine's philippia is nothing but a mixture of yttria and terbia.

### Mosandra.

62. The chemical characters of this earth are so little known that I could not attempt to search for it. But as the citron band-forming earth always appeared concentrated amongst those whose double sulphates were most soluble in potassic sulphate,—and, of these, amongst those having the palest colour and lowest atomic weight,—it was scarcely conceivable that the earth I was in search of should ultimately prove to be one whose properties did not in any case correspond to these,— of a dark orange yellow colour, forming a difficultly soluble double potassic sulphate, and having the very high equivalent of $M = 51\cdot2$; these being the properties ascribed to mosandra by the discoverer, Professor Lawrence Smith.

### Separation of terbia and yttria from erbia, holmia, and thulia.

63. The mother-liquors, from which as much terbic formate as possible had been separated by the process above described (56, 57), were now evaporated down with nitric acid till all the formates were decomposed, and the highly acid solutions of nitrates were fractionally precipitated with oxalic acid (51, 52, 53).

64. The erbic, holmic, and thulic oxalates come down first; then the terbic oxalate; lastly the yttric oxalate (53). After repeated fractional precipitations I at last succeeded in obtaining a mixture of yttria and terbia of a golden colour, which gave a very brilliant phosphorescent spectrum in the radiant matter tube, but showed no trace of absorption band when the concentrated solution. of the nitrates was examined in the spectroscope.

### Separation of terbia and yttria.

65. The crude yttria was now added to the mixture of earths (54) having a hydrogen equivalent $M = 33$, and the whole submitted again to fractionation with oxalic acid, in a somewhat modified manner.

An excess of strong nitric acid was added to the solution of mixed terbic and yttric nitrates, and the solution was heated to the boiling point. Strong oxalic acid solution was added drop by drop till a faint permanent precipitate was produced. Strong nitric acid was now added, a drop at a time, till the solution again became clear, and the whole was allowed to cool very slowly without agitation. On cooling, an oxalate crystallised out in brilliant prisms. These contained nearly all the terbia with some of the yttria, whilst the mother-liquor contained most of the yttria with a little terbia. The filtrate was treated with more oxalic acid, a fresh crop of crystals being produced,

* ' Jour. Chem. Soc.,' vol. 41, p. 277.

when the crystals were ignited, and the resulting earths re-treated with nitric acid and oxalic acid. After repeated fractionations I finally obtained in this manner a perfectly white yttria and a terbia containing a small quantity of yttria. This terbia was added to the crude terbia from previous operations, and purified as already described (57).

These operations gave me two earths,—yttria and terbia,—which, from the constancy of their H equivalents, were taken to be pure. The earths giving absorption spectra and having H equivalents other than 29·7 and 49·5, include erbia, holmia, and thulia. This portion was not further examined for the purposes of this investigation.

## *Ytterbia.*

66. Before considering it finally proved that the substance forming the citron-band spectrum was yttria, it was necessary to prepare ytterbia and ascertain its behaviour in the radiant matter tube, this earth and yttria being the only remaining earths to which the citron spectrum could possibly belong.

The two metals have hydrogen equivalents—ytterbium 57·9 and yttrium 29·7. The chemical reactions are also sufficiently different to render their separation a matter of no very great difficulty.

67. Gadolinite is said by NILSON to contain most ytterbia, so this mineral was chosen in preference to samarskite. The crude earths were first purified from all the earths whose sulphates are difficultly soluble in potassic sulphate (22, 25, 31 to 36), then by the formic acid process from terbia (56, 57), and lastly by fractional precipitation with oxalic acid from the erbia earths (65). There remained an almost white yttria, which gave the citron-band spectrum very brilliantly. Now, gadolinite contains only about 0·1 per cent. of ytterbia, and about 35 per cent. of yttria; therefore the ytterbia to yttria in this mixture was somewhat in the proportion of 1 to 300, and it gave the citron-band spectrum as brillantly as I had ever seen it. The probability was that the earth forming nearly the whole was the one giving the spectrum.

68. Ytterbic nitrate decomposes on fusion almost as easily as erbic nitrate (60), whilst yttric nitrate resists decomposition much more energetically.* Fusion of the nitrates is also the best process for throwing out the erbia, holmia, and thulia, and is therefore the best for purifying gadolinite yttria, as this mineral is rich in the erbia earths and contains little terbia.

The gadolinite yttria was converted into nitrate, fused for a short time, and extracted with water. The portions soluble and insoluble in water were again separately submitted to this treatment, until at last a colourless earth was obtained, the nitrate of which decomposed easily on fusion, and another whose nitrate resisted decomposition when exposed for a long time to nearly a red heat (70).

The earth from the easily decomposed nitrate gave at first a faint citron-band

* MARIGNAC, 'Comptes Rendus,' vol. 90, p. 902.

spectrum, evidently due to impurity. On repeating the operation several times I at last succeeded in obtaining a white earth which gave only the merest trace of citron-band spectrum. Its hydrogen equivalent, 58·0, and its chemical properties showed that it was probably MARIGNAC's ytterbia. Subsequent experiments satisfied me that this earth did not contain more than 1-10,000th part of yttria (84, 87). The extreme tediousness of the chemical operations necessary to obtain this high degree of purity, and the long time they require, prevented me from pushing these results beyond what was necessary to prove the special point at issue.

### Purification of yttria.

69. The white earth obtained in the operation described at par. 65 might still contain traces of terbia, together with erbia, holmia, and thulia. I had relied on the absence of absorption spectrum as proving the absence of erbia, holmia, and thulia, but this test is not a very delicate one, and a final purification was therefore attempted. The decomposition of the fused nitrates was now the process relied on for this final purification, the yttric nitrate resisting nearly a red heat without decomposition, whilst the erbic, holmic, and thulic nitrates are decomposed at a much lower temperature. The operation was carried on as described at par 60.

The yttric nitrate left undecomposed, after repeated fusions, was now fused at a higher temperature, extracted with water, filtered from insoluble residue, and the operation repeated on the filtrate. After several such operations the H equivalent of the yttria was taken at every succeeding operation, and the spectral appearance in the radiant matter tube was also examined. The equivalent gradually got down to 31·0, but the spectra did not vary very much; that from the earth of lowest equivalent being, however, the most brilliant.

70. The yttric nitrate, prepared from gadolinite and freed from ytterbia by the fusion of the nitrates (68), was converted into oxalate and ignited. The resulting yttria was quite white, and on testing in the radiant matter tube gave a spectrum absolutely identical with that given by the zircon (18), cerite (25), thorite and orangite (33, 34), and samarskite (64, 69), yttrias. Pure yttria was also prepared from yttro-tantalite, euxenite, allanite, tyrite, and also from plaster of Paris (15) and common limestone. In no case could I detect any difference in the position or intensity of the lines shown by their phosphorescent spectra.

### The phosphorescent spectrum of yttria.

71. The spectrum shown by pure ignited yttric sulphate in a radiant matter tube is one of the most beautiful objects in the whole range of spectroscopy. The lines are not so sharp as those given by spark spectra, but are more like the flame spectra

of the alkaline earths. The spectrum is best seen under low dispersion and not too narrow a slit. The accompanying cut gives an accurate map of the spectrum. I have given in line No. 1 the position of the principal FRAUNHOFER lines for comparison of position. Line No. 2 gives the position of the bands, and No. 3 the relative intensities represented by the heights of the ordinates. The numbers along the top refer to a scale of squared oscillation frequencies, or of the squared reciprocals of wave lengths.
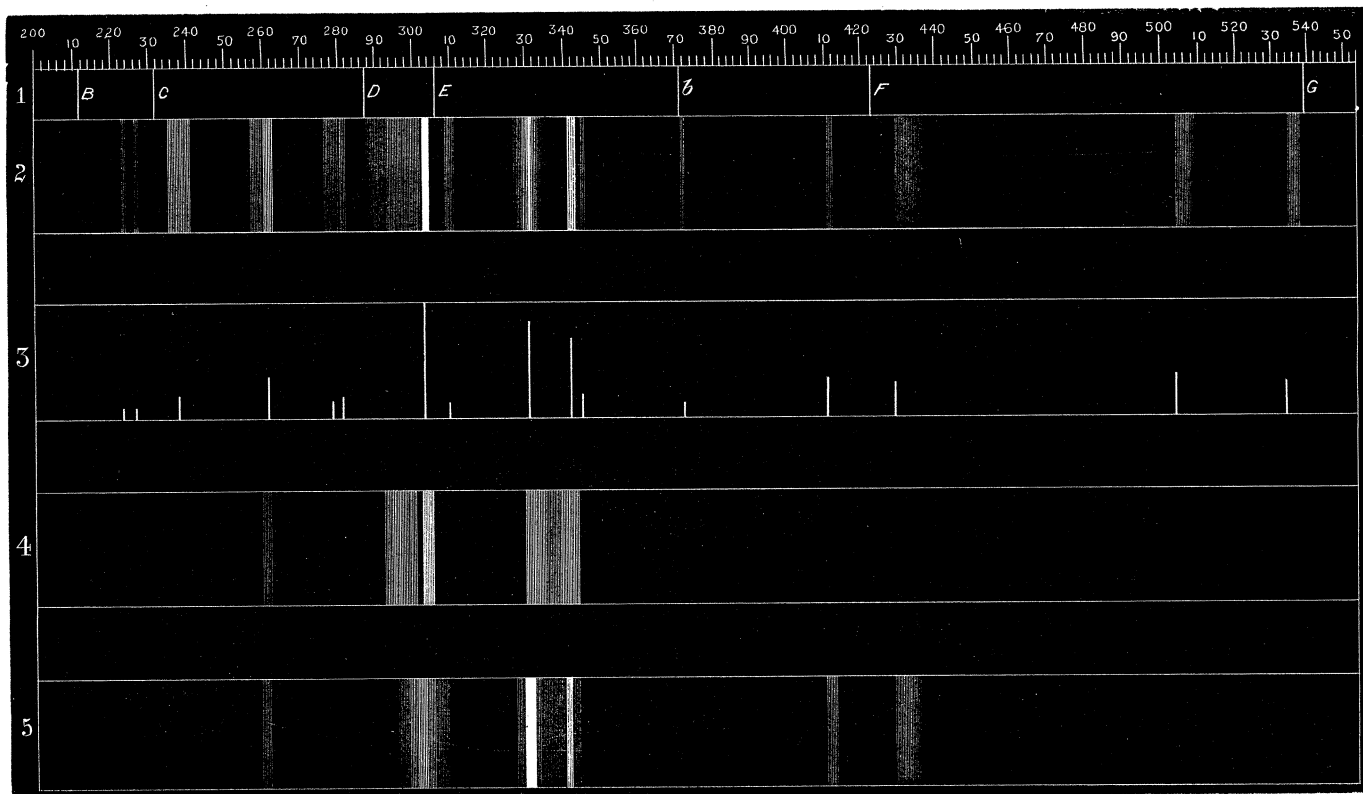


72. Commencing at the red end, two narrow faint bands are seen at 2245 and 2275, followed by a stronger and broader red band extending between 2355 and 2415. Another faint band occurs between 2577 and 2610, followed after a very narrow black interval by a stronger reddish-orange band extending to 2627. Another faint orange band occurs at about 2800, with edges too indistinct for measurement. At about 2940 a faint yellow band appears, extending to about 3025. The strong citron-coloured band follows closely from 3028 to 3049; and a little further on, between 3100 and 3120, a much fainter citron band is seen. Two characteristic green bands follow after a dark interval; the first, very bright, extending between 3312 and 3320, but shading off on each side; the second somewhat fainter, but more sharply defined than the first, extending from 3420 to 3440; there is also a third faint green band, between 3460 and 3467. At 3730 is the centre of a narrow and faint.

bluish-green band; at 4110 to 4125 in a blue band; and at 4296 another blue band commences, and, extending a short distance, fades away so gradually as to render measurement of the further side impossible. At 5052 and 5351 are two violet lines, but they are not sufficiently sharp to enable accurate measurements to be taken.

I have carefully compared the spark spectrum given by yttric chloride with the phosphorescent spectrum, and have not found any similarity between them, neither have I detected any discontinuity of spectrum on examining the faint light shown by yttrium compounds in BECQUEREL's phosphoroscope.

73. The above description applies to the spectrum shown either by pure yttria or by an earth tolerably rich in yttria. When traces are present the citron band only is seen. A little more yttria brings out the first and then the second green band, and finally, as the proportion of yttria increases, the red and blue bands appear (80 to 86).

### Circumstances modifying the yttria spectrum.

74. In the early days of this investigation I frequently found that an earthy mixture which by one mode of treatment gave no spectrum, would give a good citron band by a modification of the treatment, and I gradually found that I was most likely to get the spectrum when the body had been treated with sulphuric acid and then ignited to dull redness (4). Not knowing the circumstances governing the appearance of the citron band, it would not then have been safe to have altered this mode of treatment. Now, however, having ascertained the earth to which the spectrum was due, and having a considerable quantity at my disposal, experiments were tried on other methods of treating yttria before exposing it in the radiant matter tube.

75. Pure yttria precipitated by ammonia from the sulphate was dried at a temperature below redness and tested. It did not phosphoresce in the slightest degree, and, necessarily, no citron-band spectrum was to be seen. The yttria was removed from the tube, converted into sulphate, heated to redness, and again tested. It now gave the citron band magnificently. This shows what apparently trivial circumstances will alter the whole course of an investigation. In 1881, when searching for discontinuous phosphorescent spectra, I tried a similar experiment with pure precipitated yttria (45), and entirely missed its citron-band spectrum. Had I first treated the yttria with sulphuric acid, instead of testing the earth itself in the radiant matter tube, the results would have been very different, and this research would probably have never been undertaken.

76. Yttria was now prepared by igniting the precipitated oxalate at a red heat. On testing in the radiant matter tube it phosphoresced with feeble intensity, the light being about one-twentieth of that given by the ignited sulphate under similar conditions. The citron band was almost as sharp as the sodium line, and was shifted one division towards the blue end, now occupying the position 3050 to 3060, its

former place 3028 to 3049 being quite dark. The appearance is shown in line No. 4. On superposing this spectrum and that from the ignited sulphate the displacement of the citron bands was clearly observed; with a very narrow slit the two bands were seen not to touch. The two green bands were visible, but very hazy and indistinct, and only to be resolved into bands with difficulty. The yttria was now removed from the tube, ignited to a bright red heat, and re-tested. The spectrum was a little stronger than that given by the yttria ignited at a lower temperature, but in other respects the general appearance and measurements were unchanged. No alteration was caused by subsequent ignition to a white heat.

77. Pure yttric sulphate ignited to a bright white heat gave a spectrum corresponding to the oxide (76); the sulphate having been decomposed by the high temperature.

78. Yttric phosphate was precipitated, washed, and dried at a heat below redness, and introduced into the radiant matter tube. It phosphoresced faintly, giving the citron band hazy and faint, extending from about 3010 to 3060. The red bands were faint, and the green bands, especially the first one, were stronger than usual. The salt was now removed from the tube, and heated to redness. It became of a grey colour, and now phosphoresced with a beautiful green light. The citron band was still broad and faint, but the green bands were very bright and distinct, and the red band between 2610 and 2627 was also stronger. The spectrum No. 5 shows the appearance.

Heating the phosphate before the blowpipe made little change in the character of the phosphorescence. It was moistened with sulphuric acid, heated to a dull redness, and then tested, but no further change was produced in the spectrum. This experiment shows that the citron-band test for yttrium is far less delicate in the presence of phosphoric acid than in its absence.

## Occurrence of yttria in Nature.

79. It is an old and probably a true saying that every element could be detected everywhere had we sufficiently delicate tests for it. Early observations (10, 16) had prepared me for the wide distribution of the element giving the citron band, and no sooner had the exquisite sensitiveness of this spectrum test forced itself on my notice than I sought for yttrium in other minerals. Facts which I had noticed in connexion with the variation of the appearance of the citron spectrum, according to the quantity of yttrium present, showed that it might be possible to devise a process for the rough quantitative estimation of yttrium, and after several experiments this was ultimately carried out in the following manner :—

The calcic carbonate which was found to give no citron band (12) was boiled in a quantity of nitric acid insufficient to dissolve it. The solution was filtered from the insoluble residue, diluted to a convenient bulk, and standardised : 14·91 grains of

solution contained 1 grain of calcium. This operation was performed in a room in which had been no yttria compound, and the chemicals and apparatus were new, and had not been taken into the general laboratory. A portion of the standard solution was precipitated with ammonic oxalate, and the calcic oxalate ignited and treated with sulphuric acid. Tested in the radiant matter tube it gave no citron band.

Pure yttric sulphate was dissolved in water to such a strength that 3,000 grains of solution contained 1 grain of yttrium.

80. The solutions were mixed together in the proportion of 1 of yttrium to 100 of calcium, evaporated to dryness, and ignited with sulphuric acid, and the residue tested in a radiant matter tube. The spectrum was bright, the citron band, the two green bands, the blue, and the red bands showed distinctly.

81. A mixture was now prepared in the proportion of 1 of yttrium to 500 of calcium, and tested as above. The citron band was strong, but the green bands were fainter ; the blue bands were still visible.

82. A mixture containing 1 of yttrium to 1000 of calcium was next prepared. In the radiant matter tube the citron band was almost as strong as in the last experiment, but the edges were not so sharp, the blue bands were faint, and the green bands had disappeared.

83. A mixture containing 1 of yttrium to 5000 of calcium tested in the radiant matter tube showed the citron band still very bright, but hazy about the edges. No other bands were seen.

84. A mixture of 1 yttrium and 10,000 of calcium was now tried. The citron band was still decided, but not at all sharp.

85. One of yttrium to 100,000 of calcium was next prepared and tested. The citron band was faint, but easily seen. It could not, however, be obtained at all sharp, and appeared broader than usual.

86. A mixture of 1 of yttrium and 1,000,000 of calcium was lastly prepared, and tested in the radiant matter tube. The citron band was very faint, but there was no mistaking its presence, and with care I have no doubt a smaller quantity than 1 in 1,000,000 could be detected. This, however, appears to be near the limit of the test.

87. These seven tubes were mounted on a board, so that connexion with the induction coil could rapidly be made to either of them ; and various minerals, &c., were prepared and tested in radiant matter tubes (10). By comparing their spectra with those of the standard tubes I could, after a little practice, determine roughly the proportion of yttrium present, supposing the test not to be interfered with by the presence of phosphoric acid (78).

88. The following are some of the most interesting results obtained in this way :—

|  |  | Parts. |
|---|---|---|
| Pink coral (one particular specimen) . . . . | One part of yttrium in | 200 |
| Strontianite . . . . . . . . . . . | One    ,,     ,, | 500 |
| Stilbite . . . . . . . . . . . | One    ,,     ,, | 500 |
| Hydrodolomite, from Vesuvius . . . . . . | One    ,,     ,, | 500 |
| Witherite . . . . . . . . . . . . | One    ,,     ,, | 1000 |
| Arragonite . . . . . . . . . . . | One    ,,     ,, | 2000 |
| Chondrodite (Humite), from Vesuvius. . . . | One    ,,     ,, | 4000 |
| Egyptian syenite (Cleopatra's Needle) . . . | One    ,,     ,, | 7000 |
| Calcite . . . . . . . . . . . . | One    ,,     ,, | 10,000 |
| Natrolite . . . . . . . . . . . | One    ,,     ,, | 10,000 |
| Ox bone . . . . . . . . . . . | One    ,,     ,, | 10,000 |
| Meionite (Vesuvius) . . . . . . . . | One    ,,     ,, | 10,000 |
| Meteorite (Alfianello, Feb. 16, 1883) . . . . | One    ,,     ,, | 100,000 |
| Brevicite . . . . . . . . . . . | One    ,,     ,, | 200,000 |
| Prehnite . . . . . . . . . . . | One    ,,     ,, | 500,000 |
| Thomsonite . . . . . . . . . . . | One    ,,     ,, | 500,000 |
| Vesbine, mixed with lava, from Vesuvius . . | One    ,,     ,, | ·700,000 |
| Dolomite . . . . . . . . . . . | One    ,,     ,, | 1,000,000 |
| Tobacco ash . . . . . . . . . . | One    ,,     ,, | 1,000,000 |
| Leucite, from Vesuvius . . . . . . . | Less than one    ,, | 1,000,000 |
| Nepheline, from Vesuvius . . . . . . | None | |
| Meteorite (Dhurmsala, 1860). . . . . . | None | |
| Analcite . . . . . . . . . . . | None | |
| Phenakite . . . . . . . . . . | None | |
| Chrysolite . . . . . . . . . . . | None | |
| Haüynite . . . . . . . . . . . | None | |
| Turquoise . . . . . . . . . . . | None | |

### *Indications of other spectrum-yielding elements.*

89. Throughout the course of this paper I have devoted myself only to the citron-band spectrum. I do not, however, wish it to be thought that no other spectra were obtained. On the contrary, I have repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band, and, more rarely, of a third spectrum distinct from the other two. These I am investigating, but not yet having obtained definite results I forbear from saying any more about them. I hope that they may bear sufficiently good fruit to be worthy of presentation at some future time to the Royal Society.